

Appendix B
Data Quality Assessment

Data Quality Assessment

The following data quality assessment includes the discussion of both laboratory and field quality control practices. The QC information is presented in the following sections: sample holding times, incubation periods, method and trip blanks, duplicate sample differences, spike recoveries, and field duplicates. Data used for this report were produced by Enseco Laboratory, Pace Laboratory, and DWR's Bryte Chemical Laboratory. Since several laboratories were used during the period covered by this report, each section is further broken down into additional sections which discuss the QC data produced by each of these laboratories. Suggestions and recommendations to help facilitate future data quality evaluations are presented at the end.

Selected samples taken between August 1987 and June 1989 were analyzed by Enseco Laboratory, located in West Sacramento, California. Enseco analyzed samples for total organic carbon, and formation potentials for bromodichloromethane, bromoform, chloroform, and dibromochloromethane. TOC samples sent to Enseco were analyzed according EPA Method 415.1. Most of the THMFP samples were analyzed according to EPA method 501. EPA Method 601 was briefly used by Enseco. A total of 249 sample batches was analyzed by Enseco.

Selected samples taken between July 1989 and December 1991 were analyzed by Pace Laboratory, located in Novato, California. Pace analyzed samples for total residual chlorine and formation potentials for bromodichloromethane, bromoform, chloroform, and dibromochloromethane. Total residual chlorine samples were quantified by EPA method 330.5. Quantification of total residual chlorine was done in order to ascertain that samples were spiked with sufficient amounts of chlorine to assure complete chemical reaction with organic constituents. Pace used EPA Method 601 to analyze THMFP. A total of 179 sample batches was analyzed by Pace.

DWR's Bryte Chemical Laboratory analyzed samples submitted by MWQI during the entire study period from August 1987 to December 1991. Bryte analyzed water samples for minerals, metals and some organics. Mineral constituents included alkalinity (EPA 310.1), arsenic (EPA 206.3), boron (USGS I-2115-85), calcium (EPA 215.1), chloride (EPA 325.2), color (EPA 110.2), dissolved solids (EPA 160.1), magnesium (EPA 242.1), pH (EPA 150.1), potassium (EPA 258.1), sodium (EPA 273.1), specific conductance (EPA 120.1), sulfate (EPA 375.2), suspended solids (EPA 160.2), and turbidity (EPA 180.1). Bryte also analyzed samples for nitrate using EPA method 353.2. Metals analyzed include barium (EPA 208.1), cadmium (EPA 213.2), chromium (EPA 218.2), copper (EPA 220.1), iron (EPA 236.1), lead (EPA 239.2), manganese (EPA 243.2), molybdenum (EPA 246.2), nickel (EPA 249.2), selenium (EPA 270.3), silver (EPA 272.2), and zinc (EPA 289.2). As for organics, Bryte analyzed trihalomethane formation potentials (EPA 502.2), organic carbon (EPA 415.1), and THM precursors¹ (ultraviolet absorbance_{254 nm}).

DWR's Bryte Chemical Laboratory is in the process of becoming more automated. During the study period, Bryte had not yet developed a documentation system for reporting QC data to DWR programs. For the study, a random set of data over the five-year study period was chosen on a quarterly basis (1 QC batch per quarter). Bryte searched their original work sheets and reported the requested QC information for the randomly chosen data. QC data were documented in a report for a total of 15 batches. The evaluation of Bryte QC data for this report was based on these 15 batches.

¹ Ultraviolet absorbance _{254 nm} developed by Dobbs, R.A., et al., Water Research, 1972, Vol.6, 1173-1180.

SAMPLE HOLDING TIMES

I. ENSECO LABORATORY

Since total organic carbon analysis does not require an incubation period, the holding times correspond to the period between when the sample is collected (date sampled) to when the sample is analyzed. This period cannot exceed 30 days or else a violation has occurred. Samples analyzed by Enseco for TOC never violated the maximum 30-day requirement. Enseco's TOC batch holding times are tabulated in Table B-1.

THMFP samples must first be spiked, held for seven days, and then quenched before analysis. This process is known as incubation. Almost all samples between 1987 and 1989 were incubated by DWR's Bryte Chemical Laboratory, prior to being sent to Enseco for THMFP analysis. However, in a few cases where Bryte was not able to perform the incubation due to equipment failure, Enseco performed this task in addition to THMFP analysis. The minimum seven-day requirement for incubation was never violated by Bryte or Enseco.

The THM holding time for Enseco is the period between when the sample is quenched to when it is analyzed. This period must be within 14 days, or else a violation has occurred (Table B-2 display Enseco THMFP batch holding times.) Eighteen sample batches analyzed for THMFP exceeded EPA's 14-day recommendation for purgeable halocarbons. The sample batch that was held the longest was analyzed after 53 days. Samples which exceeded the holding time are shaded in Table B-2.

A decision on the usability of data qualified for holding time violations will depend upon the use of data. Since THM data are used in this study for determining seasonal and long-term trends in water quality, the conclusion that sample batches which exceeded the holding time are unacceptable may be imprudent. First, DWR uses a modified THMFP test which is not identical to EPA's THMFP test. Thus, a strict application of EPA's holding time may not be appropriate in this case. Although a total of 18 batches exceeded the EPA holding time, a study of THM holding time which was documented in MWQI's June 1990, *Delta Island Drainage Investigation Report*, established that a holding period of up to 80 days may not cause a noticeable loss in THM concentrations. It is also important to note that EPA does allow for variances of holding time in cases where a chemical can be shown to be stable for longer periods of time. Lastly, method holding times developed by EPA are based on the most sensitive species which does not take into consideration the more stable analytes. Therefore, for the purpose of this report, DWR considered the THM environmental data from all 18 batches usable, with the understanding that measures will be taken to reduce or eliminate this source of possible error in future work.

II. PACE LABORATORY

Pace performed incubation in the same manner as Enseco; however, Pace always spiked, quenched and analyzed the THMFP samples. The established spike to quench period is seven days. This has been experimentally determined by MWQI and DWR's Bryte Chemical Laboratory as a sufficient time allowance for the chlorination of organics to occur.

Between July 1989 and December 1991, Pace incubated THMFP samples for eight days on four occasions. On two occasions, the batches were only incubated for six days. On one occasion, spiking

and quenching occurred on the same day. The majority of the samples (over 97 percent) were incubated properly for seven days. Incubation times are presented in Table B-3.

Overall, seven batches were not properly incubated for the specified seven-day period. Although a particular batch was reported as having been spiked and quenched on the same day, the results suggests that this was a reporting error. The rest of the violations only deviated from the prescribed seven-day period by one day. Based on the asymptotic nature of the THM formation, where the majority of the chlorination occurs within the first few days of incubation, deviation of one day would not significantly misrepresent the maximum formation potential. With this in mind, Pace's violations of incubation times by one day are acceptable.

Pace consistently reported its spiked and quenched dates; however, it has neglected to report the analysis dates. Therefore, DWR was unable to determine THMFP holding time violations for Pace.

III. DWR'S BRYTE CHEMICAL LABORATORY

A review of holding times indicates that two QC sample batches had samples that exceeded the EPA seven-day holding time for total dissolved solids analysis. However, a study performed by Bryte found that filtered samples can be held up to three months without significant loss of total dissolved solids. No samples exceeded the three-month holding time. No other holding times were exceeded. For the purpose of this study, TDS samples that exceeded the seven-day holding limit can be considered acceptable. However, measures will be taken to reduce or eliminate this possible source of error in future work.

TABLE B-1: ENSECO TOC BATCH HOLDING TIMES*

BATCH LOT #	DATE SAMPLED	DATE ANALYZED	HOLDING TIME	BATCH LOT #	DATE SAMPLED	DATE ANALYZED	HOLDING TIME
31219	9-2-87	9-17-87	15	41268	4-28-88	5-2-88	4
31278	9-9-87	9-17-87	8	41325	5-3-88	5-4-88	1
31539	9-24-87	9-25-87	1	41534	5-9-88	5-17-88	8
31791	10-8-87	10-15-87	7	41619	5-19-88	5-25-88	6
31981	10-22-87	10-26-87	4	41732	5-26-88	6-6-88	11
32054	10-28-87	10-30-87	2	41909	5-26-88	6-15-88	20
32136	11-3-87	11-5-87	2	42008	6-14-88	6-20-88	6
32177	11-5-87	11-10-87	5	42122	6-22-88	6-23-88	1
32448	11-24-87	12-15-87	21	42328	7-6-88	7-7-88	1
32506	12-1-87	12-15-87	14	42411	7-12-88	7-13-88	1
32611	12-8-87	12-28-87	20	42419	7-12-88	7-14-88	2
32759	12-16-87	1-4-88	19	42444	7-14-88	7-15-88	1
32983	1-6-88	1-15-88	9	42573	7-20-88	7-27-88	7
32999	1-7-88	1-11-88	4	41263	4-27-88	5-2-88	5
33210	1-21-88	2-16-88	26	42726	8-1-88	8-9-88	8
33219	1-21-88	2-16-88	26	42846	8-9-88	8-19-88	10
40667	2-10-88	2-11-88	1	42916	8-10-88	8-25-88	15
40196	2-18-88	2-24-88	6	42985	8-16-88	8-25-88	9
40267	2-23-88	2-25-88	2	43027	8-17-88	8-26-88	9
40550	3-7-88	3-14-88	7	43149	8-24-88	9-7-88	14
40587	3-15-88	3-16-88	1	43254	8-31-88	9-15-88	15
40655	3-18-88	3-22-88	4	43303	9-6-88	9-19-88	13
40722	3-23-88	3-25-88	2	44664	11-30-88	12-14-88	14
40924	4-5-88	4-8-88	3	44741	12-6-88	12-19-88	13

* The EPA holding time for Method 415.1 is 28 days.

B-6

D-054680

BATCH LOT #	DATE SAMPLED	DATE ANALYZED	HOLDING TIME	BATCH LOT #	DATE SAMPLED	DATE ANALYZED	HOLDING TIME
41079	4-15-88	4-22-88	7	44785	12-7-88	12-14-88	7
41185	4-18-88	4-25-88	7	44865	12-13-88	12-19-88	6
44965	12-20-88	12-21-88	1	45184	1-9-89	1-10-89	1
45004	12-21-88	12-28-88	7	45201	1-10-89	1-12-89	2
45070	12-28-88	1-4-89	7	47977	6-26-89	7-17-89	21
45124	1-3-89	1-5-89	2	47986	6-28-89	7-17-89	19
45145	1-5-89	1-6-89	1	48025	6-29-89	7-8-89	9
45166	1-6-89	1-9-89	3	48042	6-30-89	7-8-89	8

B-7

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* The EPA holding time for Method 415.1 is 28 days.

TABLE B-2: ENSECO THMFP BATCH HOLDING TIMES*

BATCH LOT	DECHLORINATION DATE	DATE ANALYZED	HOLDING TIME	BATCH LOT	DECHLORINATION DATE	DATE ANALYZED	HOLDING TIME
30959	9-8-87	9-8-87	0	041787	5-27-88	6-15-88	19
31219	9-3-87	9-15-87	12	041910	6-7-88	6-16-88	9
31324	9-11-87	9-24-87	13	042096	6-21-88	6-24-88	3
31685	10-2-87	10-19-87	17	042154	6-23-88	6-30-88	7
32022	10-27-87	11-4-87	8	042273	6-30-88	7-1-88	1
32136	11-3-87	11-9-87	6	042410	7-12-88	7-13-88	1
32227	11-9-87	12-6-87	27	042445	7-14-88	7-18-88	4
32321	11-16-87	11-27-87	11	042912	8-11-88	8-16-88	5
32520	12-2-87	12-4-87	2	043019	8-18-88	8-19-88	1
32725	12-14-87	1-7-88	24	043076	8-22-88	8-25-88	3
32859	12-22-87	1-20-88	29	043108	8-24-88	8-25-88	1
32860	12-22-87	1-11-88	20	043199	8-29-88	9-9-88	11
32908	12-28-87	1-28-88	31	043316	9-7-88	9-12-88	5
33118	1-15-88	3-3-88	47	043448	9-15-88	9-20-88	5
33444	2-3-88	3-28-88	53	043471	9-16-88	9-21-88	5
040197	2-18-88	3-26-88	36	043572	9-23-88	9-26-88	3
040342	2-29-88	4-1-88	32	043689	10-3-88	10-6-88	3
040411	3-2-88	4-7-88	36	043915	10-13-88	10-17-88	4
040724	3-23-88	4-18-88	26	044095	10-24-88	10-27-88	3
040758	3-25-88	4-14-88	20	044165	10-28-88	11-10-88	13
040872	4-1-88	5-5-88	32	044336	11-10-88	11-18-88	8
041043	4-13-88	4-26-88	13	044501	11-18-88	11-28-88	10

*According to EPA Method 501 and 601, the holding time (from quench to analysis) is 14 days.

BATCH LOT	DECHLORINATION DATE	DATE ANALYZED	HOLDING TIME	BATCH LOT	DECHLORINATION DATE	DATE ANALYZED	HOLDING TIME
041204	4-25-88	5-8-88	13	044613	11-29-88	12-5-88	6
041441	5-9-88	5-30-88	21	044853	12-2-88	12-16-88	14
041495	5-12-88	6-8-88	27	044890	12-15-88	12-29-88	14
041669	5-23-88	6-10-88	18	044923	12-16-88	12-27-88	11
045073	12-29-88	1-4-89	6	046029	3-6-89	3-8-89	2
045308	1-17-89	1-18-89	1	046043	3-15-89	3-20-89	5
045465	2-6-89	2-9-89	3	046065	3-16-89	3-21-89	5
045501	2-8-89	2-10-89	2	046117	3-15-89	3-22-89	7
045504	1-31-89	2-1-89	1	046170	3-21-89	3-23-89	2
045562	2-13-89	2-13-89	0	046384	4-6-89	4-7-89	1
045582	2-15-89	2-17-89	2	046546	4-14-89	4-14-89	0
045611	2-15-89	2-18-89	3	047977	6-27-89	7-7-89	10
045741	2-23-89	2-23-89	0	047985	6-28-89	7-7-89	9
045932	3-8-89	3-9-89	1	048005	6-29-89	7-8-89	9

B-9

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*According to EPA Method 501 and 601, the holding time (from quench to analysis) is 14 days.

TABLE B-3: PACE INCUBATION TIMES

PROJECT #	BATCH CHLORINATION	BATCH DECHLORINATION	HOLDING TIME (DAYS)	PROJECT #	BATCH CHLORINATION	BATCH DECHLORINATION	HOLDING TIME (DAYS)
400711508	7-20-90	7-27-90	7	401213501	1-9-91	1-19-91	7
400717502	7-23-90	7-30-90	7	410107503	1-25-91	2-1-91	7
400801506	8-6-90	8-13-90	7	410118507	2-1-91	2-8-91	7
400809503	8-21-90	8-28-90	7	410130506	2-20-91	2-27-91	7
400814506	8-31-90	9-7-90	7	410215503	3-8-91	3-18-91	7
400821501	9-13-90	9-20-90	7	410228505	3-13-91	3-20-91	7
*400823506	10-1-90	10-8-90	7	410314500	3-26-91	4-2-91	7
*400823506	10-2-90	10-9-90	7	410402505	4-5-91	4-12-91	7
*400826506	10-2-90	10-2-90	0	410411507	4-12-91	4-19-91	7
400830502	10-10-90	10-17-90	7	410419504	4-26-91	5-3-91	7
400906504	10-15-90	10-22-90	7	410424500	4-26-91	5-3-91	7
400912502	10-17-90	10-24-90	7	410426505	5-3-91	5-10-91	7
400919507	10-22-90	10-29-90	7	410515505	4-18-91	4-25-91	7
400926506	10-24-90	10-31-90	7	410523501	5-24-91	5-31-91	7
401004504	10-30-90	11-6-90	7	410614505	6-21-91	6-28-91	7
401012509	11-1-90	11-8-90	7	410701507	7-11-91	7-18-91	7
401018502	11-15-90	11-23-90	8	410814502	8-16-91	8-23-91	7
401023505	11-20-90	11-27-90	7	410822504	8-22-91	8-29-91	7
*401025507	11-20-90	11-27-90	7	410916505	9-17-91	9-24-91	7
*401025507	11-26-90	12-3-90	7	411016513	10-17-91	10-24-91	7
401044504	10-30-90	11-6-90	6	411025505	10-31-91	11-7-91	7
401101505	11-29-90	12-6-90	7	411122500	12-6-91	12-13-91	7
401115504	12-3-90	12-10-90	7	411212513	12-26-91	1-2-92	7
411212514	1-6-91	1-13-91	7	490728511	8-7-89	8-15-89	8
490726507	8-2-89	8-9-89	7	490728512	8-7-89	8-15-89	8
490726508	8-2-89	8-9-89	7	490728513	8-9-89	8-16-89	7
490726509	8-2-89	8-9-89	7	490728514	8-9-89	8-16-89	7

B-10

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D-054684

B-11

PROJECT #	BATCH CHLORINATION	BATCH DECHLORINATION	HOLDING TIME (DAYS)	PROJECT #	BATCH CHLORINATION	BATCH DECHLORINATION	HOLDING TIME (DAYS)
490728507	8-3-89	8-10-89	7	490728515	8-9-89	8-16-89	7
490728508	8-4-89	8-10-89	6	490728516	8-15-89	8-22-89	7
490728509	8-3-89	8-10-89	7	490731506	8-15-89	8-22-89	7
490728510	8-7-89	8-15-89	8	490804506	8-29-89	9-5-89	7

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METHOD BLANKS

Method blanks are laboratory samples that have unmeasurable, negligible, or acceptable low amounts of the analytes of interest. Their purpose is to detect and measure sample contamination introduced through sample preparation or analysis procedures. If a method blank sample shows nondetect, the samples associated with the batch are assumed to be free of contamination. In some cases method blanks may show acceptable detectable concentrations which are commonly referred to as "noise" or "instrument background" levels.

I. ENSECO

Enseco analyzed 407 method blanks for bromodichloromethane, bromoform, chloroform, dibromochloromethane, and total organic carbon. No detectable concentrations of analytes were measured in any of the method blanks.

II. PACE

There were 672 method blank analyses performed by Pace. Total Residual Chlorine (TRC) appeared regularly in blanks (118 out of 121 TRC samples analyzed). In this case, the TRC analyses were designed to show if method blanks were treated with enough excess chlorine to convert as much of the THM precursors into THM as possible. When TRC is not detected, the question arises if a sufficient amount of chlorine was added to adequately react to produce THMs. Only 141 blanks were analyzed positive for THMs. These THM results are presented in the table B-4 to show their relative distribution and the frequency of detection.

Table B-4: Distribution and Detection Frequency of Pace Method Blanks

Analytes	Method Detection Limit*	Blank Analyses Performed	Positive Blanks	Frequency
Bromodichloromethane	0.5 µg/L	136	0	0%
Bromoform	0.5 µg/L	137	0	0%
Chloroform	0.5 µg/L	141	141	100%
Dibromochloromethane	0.5 µg/L	137	0	0%
Total Residual Chlorine	1 mg/L	121	118	98%

*EPA method 501

There are three possible reasons for elevated chloroform in the blank analyses. First, trace organics may have existed in the method blank water and could have acted as a precursor for THMs in the blank. In fact, Pace often reported that "low purity or unpurged" water was used in their method blanks as an explanation for high blank results. The excess chlorine and negligible concentration of bromide in the blank solution would result in chemical conditions which favor the formation of chloroform. However, unless organic-free blank water is used, chloroform which resulted from contaminated blank water cannot be differentiated from chloroform which was introduced as actual contamination elsewhere in the process.

Second, chloroform itself could have been introduced from the chlorine solution being used to spike the samples. However, based on the concentrations of chloroform found in the blanks, and the fact that the spike volume accounts for only two percent of the total blank volume, the chlorine spike solution would have to contain chloroform at concentrations as high as 90 mg/L in some cases. Thus, it is unlikely that chloroform from the spike solution would be a major contributor.

Third, chloroform could have contaminated the sample between quenching and prior to analysis. This should result in a positive bias in THMFP in all samples. However, there are many samples where the blank exceeds the total THMFP in the batch environmental samples. This suggests that little or no detectable contamination is occurring after the quenching of environmental samples.

In conclusion, method blank analyses of THMFP by Pace were done incorrectly. Notes made by the analysts suggested that low purity water was often used. Even the incubation of "cleaner" blank water used by Pace for THMFP (where analyst's note of low purity water was not made) consistently displayed chloroform concentrations with an average of about 30 $\mu\text{g/L}$. Spiking of organic-free water with chlorine by Bryte Laboratory shows that chloroform is typically found at levels below 5 $\mu\text{g/L}$. Moreover, Enseco never found THMs in their method blanks (MDL = 1 $\mu\text{g/L}$). All 551 method blank analyses from Pace were, thus, considered invalid and unusable.

Pace's THMFP environmental samples were probably not contaminated by the tainted blank water, since analytical procedures did not require the use of method blank water in the preparation of environmental samples. Furthermore, the majority of THMFP samples have concentrations of THMs which are considerably high (hundreds to thousands of $\mu\text{g/L}$). Therefore, we consider the environmental THMFP data to be acceptable.

MATRIX SPIKE RECOVERY

Matrix spikes are known concentrations of analytes added to a sample prior to sample preparation. Thus, matrix spike recoveries are used to assess potential recovery bias caused by matrix interferences or analytical limitations. The recovery of the matrix spike indicates the accuracy of the analytical measurement system. Recovery limits are used to evaluate the acceptable range of matrix spike concentrations.

I. ENSECO

Enseco performed 132 matrix spike analyses. Enseco did not report matrix spike recovery limits for TOC or THMs. Instead, Enseco's laboratory control sample recovery limits for EPA Method 501 was used to help evaluate the relative quality of the recoveries. Typically, the acceptable matrix spike recovery range is wider than the LCS range due to the greater variability in measurement caused by matrix interferences. Thus, the use of an LCS recovery range tends to be conservative. The frequency of recovery limit exceedances is shown in Table B-5:

Table B-5: Distribution and Frequency of LCS Recovery Limit Exceedances for Enseco Matrix Spikes

Analytes	LCS Recovery Limit*	Matrix Spikes Performed	Samples Outside of Recovery Limits	Frequency
Total Organic Carbon	85-111%	1	0	0%
Bromodichloromethane	80-125%	38	6	16%
Bromoform	80-125%	30	13	43%
Chloroform	80-125%	36	7	19%
Dibromochloromethane	80-125%	27	10	37%

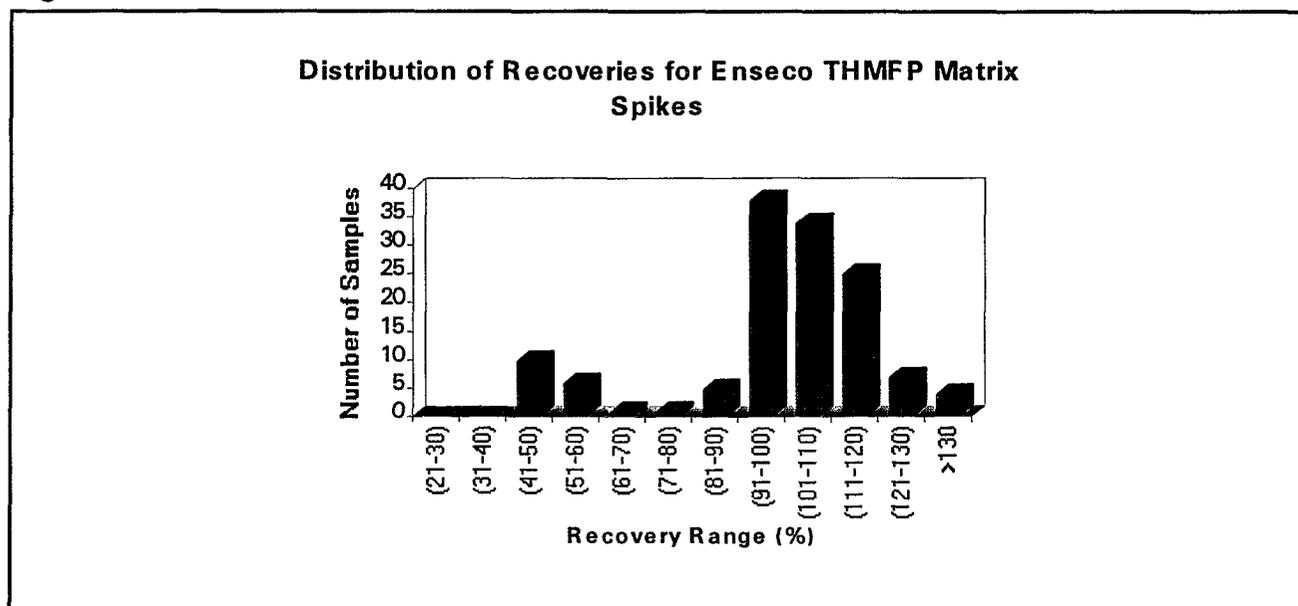
* EPA Method 501. No matrix spike recovery ranges were given.

Exceedance of the LCS recovery limits occurred in all parameters except for TOC (only one matrix spike for TOC was performed). It should be noted that one of the chloroform samples had been spiked incorrectly, that is, the environmental concentration was greater than the spike concentration. EPA recommends that the spike concentration be 1-5 times the concentration of the environmental sample. In addition, 14 samples had been spiked at greater than 5 times the environmental sample concentrations. Quantification of recoveries may be inaccurate since the measurement uncertainty of the larger spiked concentration may be greater than the value of the much smaller environmental concentration.

Overall, 73 percent of THMFP matrix spikes is within the LCS recovery limits used. Since matrix spike recovery limits are not available, we cannot develop any conclusion on recovery bias. Recovery results from Enseco shows that bromoform and dibromochloromethane are significantly more difficult to recover than chloroform and bromodichloromethane. This distinction parallels that of EPA's recommended LCS recovery limits (CFR40, Pt.136, App.A) which shows that bromoform

and dibromochloromethane have considerably larger acceptance ranges than the other two THM species. The distribution of recoveries for Enseco THMFP matrix spikes is plotted in Figure B-1:

Figure B-1



II. PACE

Pace performed 558 matrix spike analyses. Like Enseco, Pace did not report any matrix spike recovery limits. Thus, Pace's LCS recovery limits which are more conservative than matrix spike recovery limits will be used instead as the criteria. The frequency of LCS recovery limit exceedances is shown in the Table B-5:

Table B-5: Distribution and Frequency of LCS Recovery Limit Exceedances for Pace Matrix Spikes

Analytes	LCS Recovery Limit*	Matrix Spikes Performed	Samples Outside of Recovery Limits	Frequency
Bromodichloromethane	65-135%	140	12	9%
Bromoform	65-135%	137	6	4%
Chloroform	65-135%	140	38	27%
Dibromochloromethane	65-135%	141	5	4%

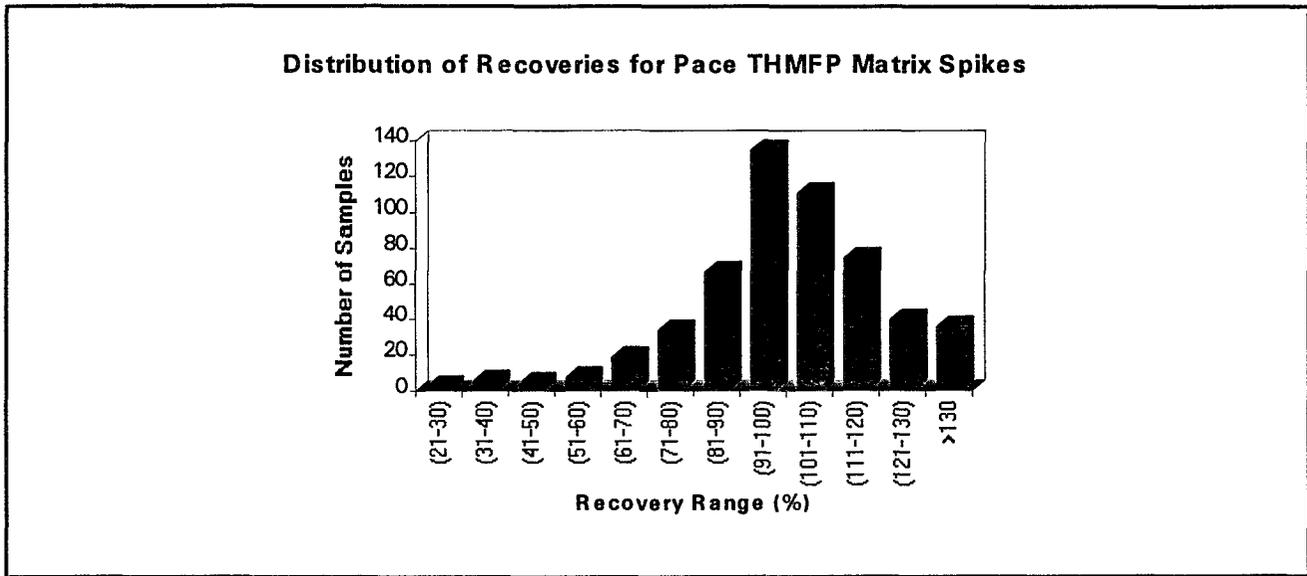
*EPA Method 601. No matrix spike recovery ranges were given.

Pace's LCS recovery limit exceedances are less frequent than those of Enseco for matrix spikes. This is likely due to the broader acceptable range for EPA Method 601 that we have used for Pace (65-135 percent). Overall, 89 percent of Pace's matrix spike analyses are within the acceptable LCS ranges used. The determination of proper spiking concentrations by Pace could not be determined due to the

lack of information provided by the laboratory. The percent recovery for each spike was reported, but the spike concentration and the initial environmental concentration were not given.

Pace's THM recoveries are plotted in Figure B-2. Note that Pace's THM recoveries are more normally distributed than Enseco THM recoveries. Recovery bias cannot be determined due to the lack of matrix spike recovery limits. In contrast to Enseco, Pace's recovery illustrates that chloroform and bromodichloromethane are much harder to recover than bromoform and dibromochloromethane. Pace's samples may have been contaminated.

Figure B-2



III. BRYTE

Bryte performed matrix spikes for all analytes (see first page of Appendix B) except EC, pH, TDS, TOC and UVA. Review of the results indicated only one batch had recovery results below the matrix spike recovery limit. The batch was found to have chloride recovery below the limits of 89-114 percent. Two spikes were included in the batch, with recoveries of 87 and 88 percent. These recoveries are only slightly below the control limits; therefore, they are usable for the MWQI study. However, the data are considered to be estimated due to potentially low bias. No other spike recoveries for any other parameter were found to be outside their control limits.

LABORATORY CONTROL SAMPLE RECOVERY

Laboratory control samples (LCS) are prepared by spiking known concentrations of analytes into a clean medium such as ultra-pure distilled water. In the case of THMs, the samples are then taken through preparation and analysis. LCS results are used to assess the accuracy of the measurement system. LCSs are not designed to provide information about the potential matrix bias.

I. ENSECO

Enseco performed 343 LCS recovery spikes. The TOC spike recovery limit used by Enseco is 85-111 percent. The Enseco THM spike recovery limit is 65-135 percent. A summary of LCS spike recovery results is shown in the Table B-7:

Table B-7: Distribution and Frequency of LCS Recovery Limit Exceedances for Enseco LCS Spikes

Analytes	LCS Recovery Limit*	LCS Spikes Performed	Samples Outside of Recovery Limits	Frequency
Total Organic Carbon	85-111%	89	0	0%
Bromodichloromethane	80-125%	70	6	9%
Bromoform	80-125%	58	13	22%
Chloroform	80-125%	69	7	10%
Dibromochloromethane	80-125%	57	10	18%

*EPA Method 501.

TOC recoveries never exceeded the LCS recovery limit. Moreover, the TOC spikes showed good recovery with most of the results between 91 and 100 percent (as shown in Figure B-3.)

Figure B-3

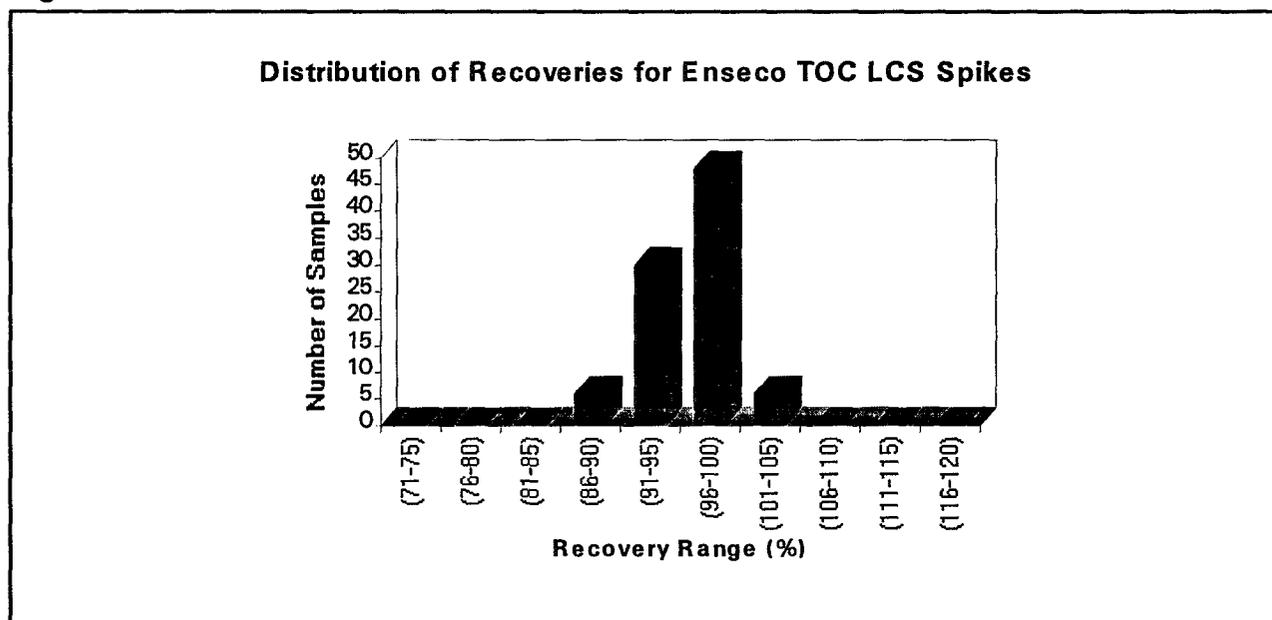
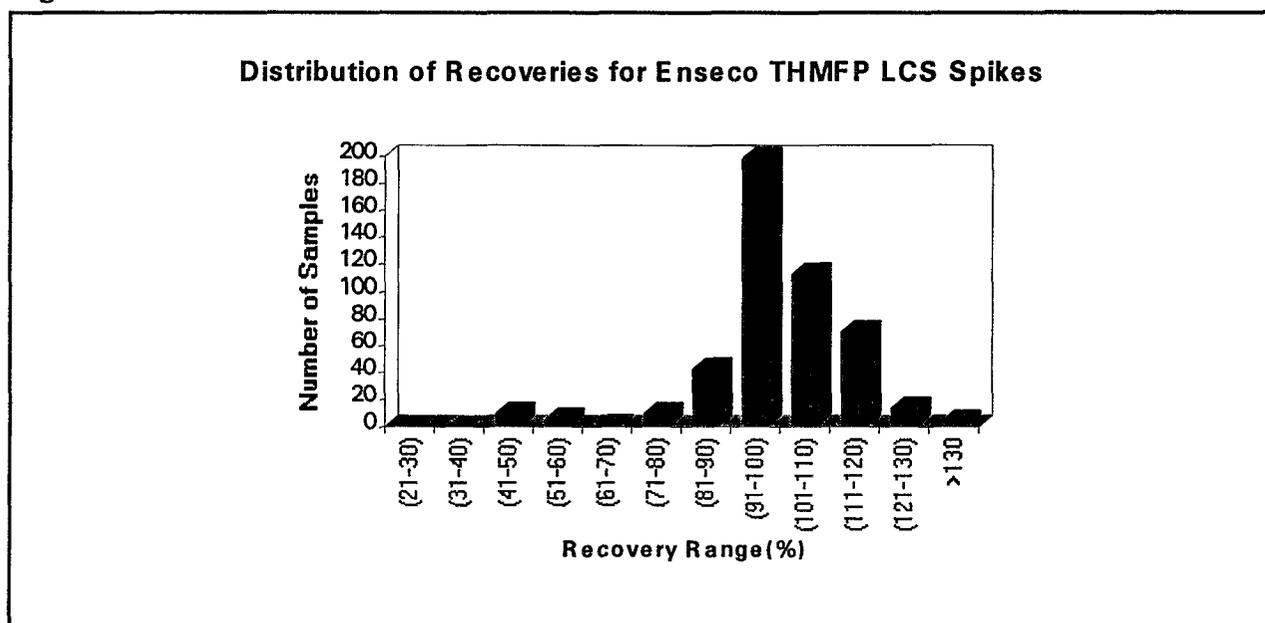


Figure B-4



THM LCS spike recovery distribution is shown in Figure B-4. Overall, 86 percent of Enseco's THM LCS spikes were within the acceptable LCS recovery limits. Recovery limits for THMs were violated more frequently by Enseco's matrix spikes than by Enseco's LCSs likely due to matrix interferences. For matrix spikes, the frequency of recovery limit exceedances for bromodichloromethane, bromoform, chloroform, and dibromochloromethane was 16, 43, 19 and 37 percent respectively. In comparison, the frequency of recovery limit exceedances of Enseco's LCSs was 9, 22, 10 and 18 percent respectively.

II. PACE

No LCS data were provided by Pace.

III. BRYTE

Bryte used LCSs to evaluate the accuracy of the pH measurements. The pH of a LCS was measured at the beginning and the end of each batch. The difference between the initial and final reading must be within the laboratory control limit (0.24 pH units). One batch was found to slightly exceed this limit with a difference of 0.3 pH units. The sample results from this batch are considered estimates, but are useable for the MWQI study. No other LCS were performed by Bryte.

MATRIX SPIKE DUPLICATES

Matrix spike duplicates are split matrix spike samples used to assess the precision or reproducibility in the analytical procedure.

I. ENSECO

Enseco performed 132 matrix spike duplicate analyses. Relative Percent Difference limits for matrix spike duplicates were not provided by Enseco. Relative percent difference is a measure of variability, adjusted for the magnitude of concentration values. LCS RPD limits were used instead to ascertain the relative quality of these matrix spike duplicates. Note that the use of LCS precision limits is a conservative approach to assess the precision of matrix spike duplicates. Precision limits for matrix spikes tend to be more lenient than LCS samples for the same analyte. The distribution of exceedances of LCS limits is shown for TOC and THMs in Table B-8.

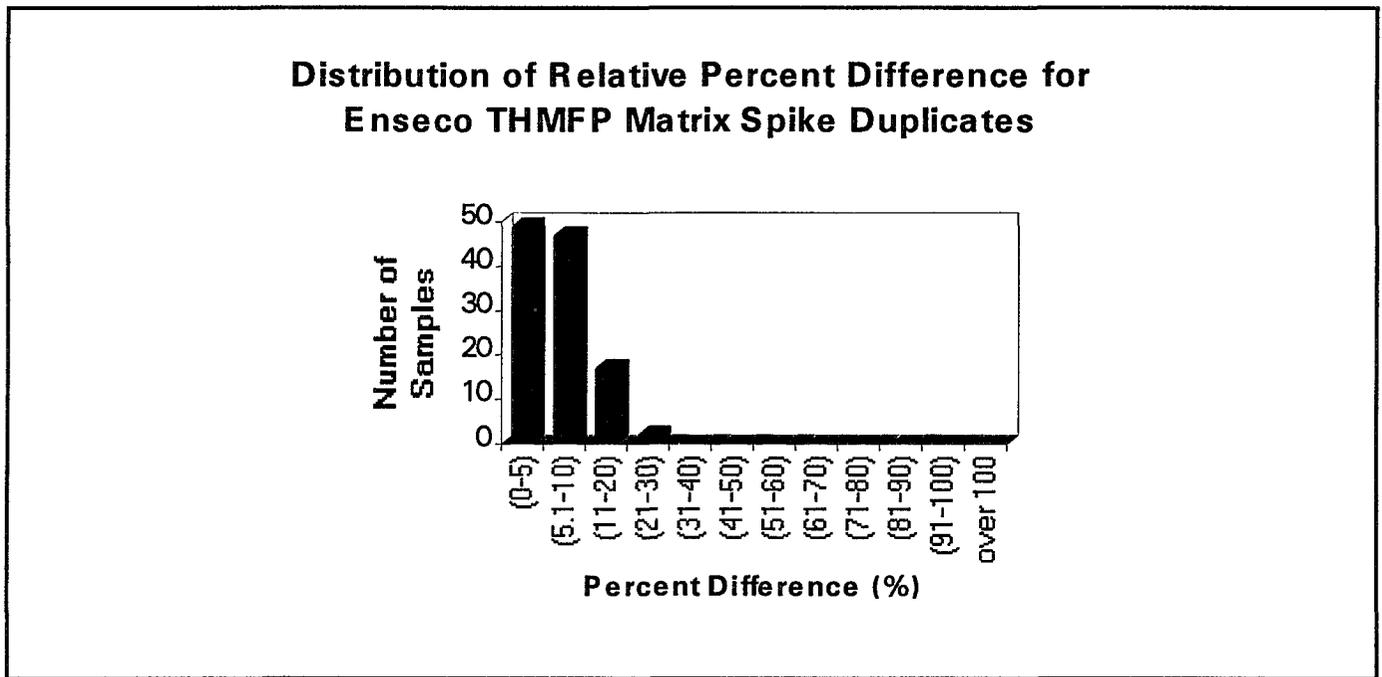
Table B-8: Distribution and Frequency of LCS Precision Limit Exceedances for Enseco Matrix Spikes Duplicates

Analyte	LCS RPD Limit*	Matrix Spike Performed	Samples Outside of RPD Limits	Frequency
Bromodichloromethane	22%	38	0	0%
Bromoform	22%	30	1	3%
Chloroform	22%	36	0	0%
Dibromochloromethane	22%	27	0	0%

* EPA Method 501. Precision limits for matrix spike duplicates were not given.

Matrix spike results strongly suggest that there is high precision for Enseco matrix spike duplicates. The only RPD which exceeded the limit is actually very close to the THM limit at 22.8 percent. Note that 16 out of the 148 matrix spikes were only analyzed once so that only one recovery value was calculated. Therefore, RPDs could not have been calculated for these samples. The precision of Enseco matrix spike duplicates is very good. The RPD distribution of THMFP samples is shown in Figure B-5.

Figure B-5



II. PACE

Pace performed 558 matrix spike duplicate analyses for THMs. Pace reported an LCS RPD limit of 35 percent in lieu of a THM matrix spike RPD limit which was unavailable. The frequency in which matrix spike duplicates are outside of the LCS RPD limit is shown in Table B-9.

Table B-9: Distribution and Frequency of LCS Precision Limit Exceedances for Pace Matrix Spike Duplicates

Analyte	LCS RPD Limit*	Matrix Spike Performed	Samples Outside of RPD Limits	Frequency
Bromodichloromethane	35	140	6	4%
Bromoform	35	137	10	14%
Chloroform	35	140	8	6%
Dibromochloromethane	35	141	5	4%
Total Residual Chlorine	25	129	6	5%

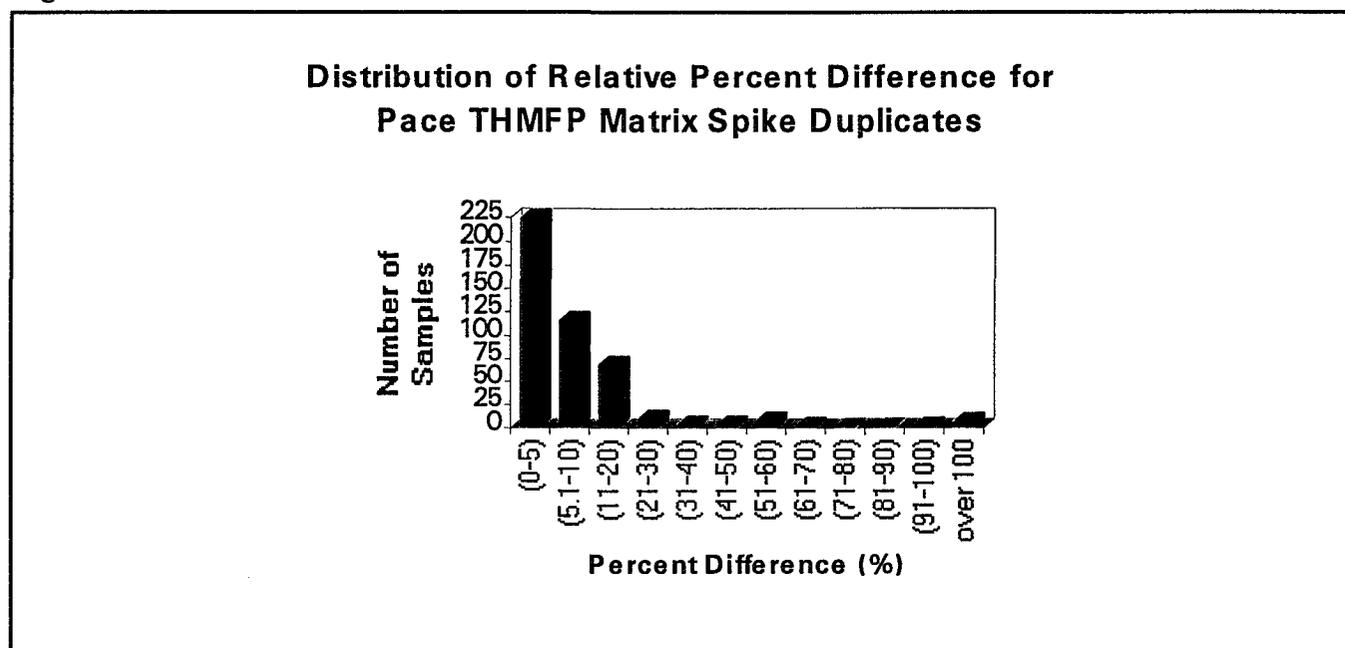
*EPA Method 601. Precision limits of matrix spike duplicates were not given.

Twenty-nine matrix spike duplicates exceeded the 35 percent RPD limit for THMs set by Pace Laboratory. These exceedances ranges from RPD values of 36 to 159 percent. Exceedances, particularly those which are fairly close to the RPD limit, are not necessary invalid but should be considered questionable. Three duplicates had slight exceedances. The remaining 26 exceedances which had RPD values of 50 percent or higher are more questionable in terms of precision. THM data in these 26 batches will be tagged and not used. The distribution of THM species in those analyses which exceeded the RPD limit is fairly well scattered among the four major species with bromoform

showing the highest frequency. This also agrees with EPA's analysis of overall precision among the four THM species. (CFR40, pt.136. App.A)

Overall, 95 percent of Pace's matrix spike duplicates have precision which fall within the LCS RPD limit used. These results are very good especially considering that LCS precision limits were used instead of matrix spike precision limits. The distribution of Pace's matrix spike duplicate precision is shown in Figure B-6.

Figure B-6



Matrix spike duplicates of total residual chlorine shows good precision with 95 percent of TRC samples being within the LCS precision limit.

III. Bryte

No matrix spike duplicates were performed by Bryte.

LABORATORY CONTROL SAMPLE DUPLICATES

Laboratory control sample duplicates are split samples of a well-characterized blank water which has been spiked with a known amount of a target analyte. They are used to assess the precision or reproducibility in the analytical system.

I. ENSECO

Enseco performed 343 LCS duplicate analyses. The distribution of LCS limit exceedances is shown in Table B-10.

Table B-10: Distribution and Frequency of LCS Precision Limit Exceedances for Enseco LCS Duplicates

Analytes	LCS RPD Limit*	LCS Duplicates Analyzed	Samples Outside of RPD Limits	Frequency
Total Organic Carbon	18%	89	0	0%
Bromodichloromethane	22%	70	1	1%
Bromoform	22%	58	5	9%
Chloroform	22%	69	0	0%
Dibromochloromethane	22%	57	0	0%

*EPA Method 501.

Overall, the measurement precision of Enseco's TOC and THM LCS duplicates is very good. None of the TOC duplicates exceeded the LCS RPD limit, and over 97 percent of the THM duplicates were within the LCS precision limit. The precision distributions of Enseco's TOC and THM LCS duplicates are shown in Figures B-7 and B-8.

Figure B-7

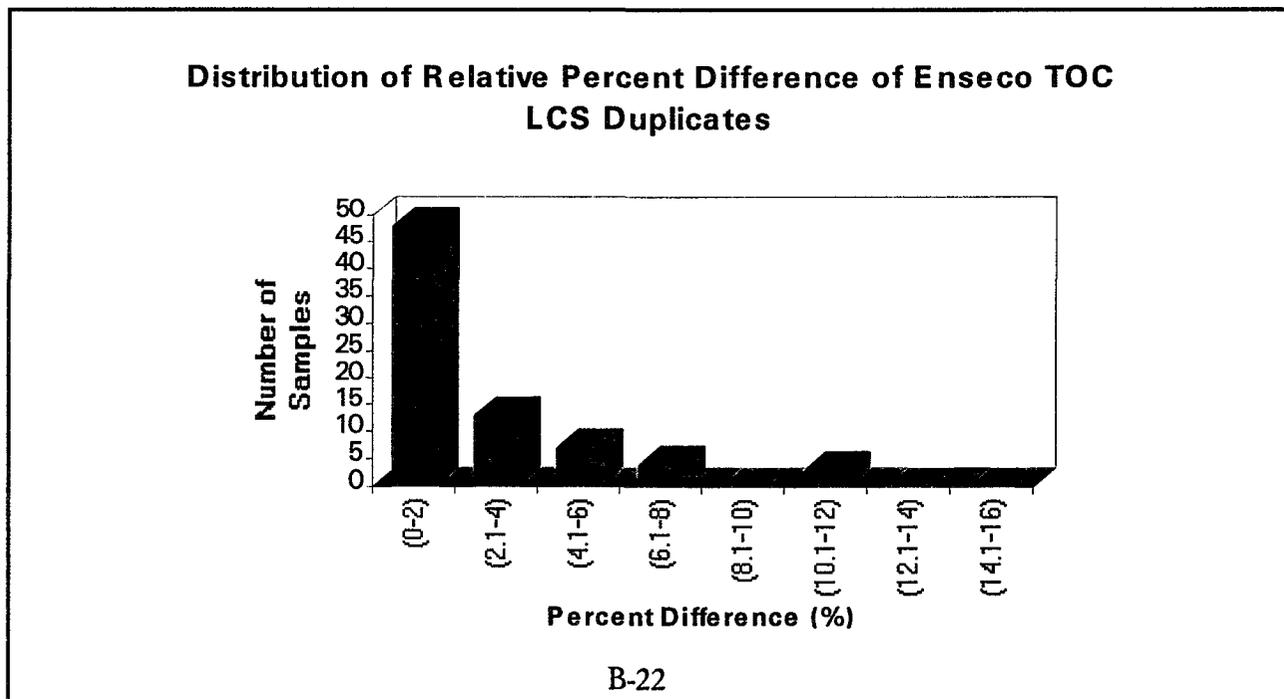
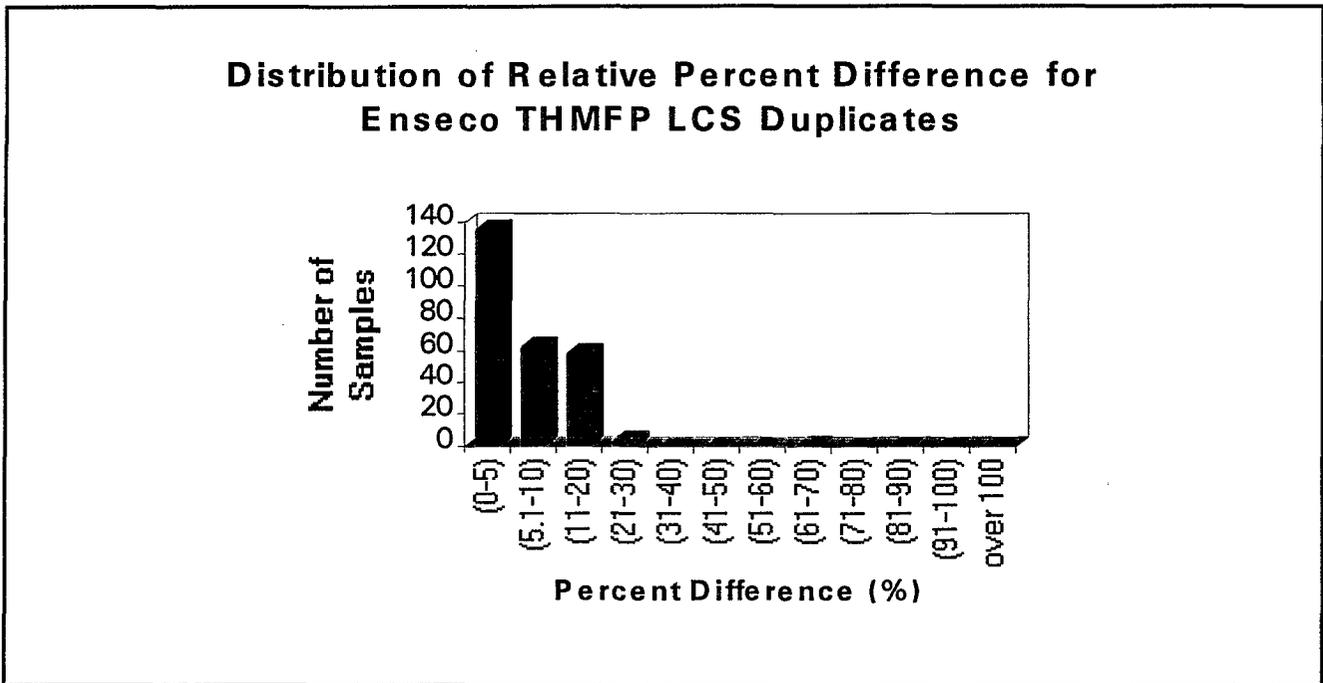


Figure B-8



Five bromoform LCS duplicate analyses exceeded the LCS RPD limit; however, all five RPD values are very close to 22 percent. These five duplicates should be tagged as questionable but still usable, because the RPD values were exceeded only slightly. As for why bromoform samples exceeded the RPD limit more frequently than do other THMs, this is likely due to the fact that the gas chromatograph detectors for EPA Method 501 and 601 are least sensitive to bromoform as compared to the other THM species. Based on duplicate results of THM matrix spikes and laboratory control samples from both Pace and Enseco, bromoform results appear to be the most difficult to reproduce.

A bromodichloromethane duplicate pair exhibited an exceedance of the 22 percent RPD limit. The RPD for this pair is 69 percent and can be considered as significant. Associated environmental data in this analytical batch will not be used.

II. PACE

No LCS data were provided by Pace.

III. BRYTE

No LCS duplicates were used by Bryte; however, Bryte evaluated the precision of the laboratory procedure by performing duplicate analyses of environmental samples. An environmental sample is split, and the results from the two samples are compared. The precision is evaluated by taking the difference of the sample results, not the RPD. The difference between duplicate samples was compared to Bryte's precision control limits. Review of the Bryte data (15 randomly selected sample batches) shows that one batch was found to have a total organic carbon duplicate sample difference of 0.38 mg/L which exceeded the precision control limit 0.3 mg/L. Since the duplicates just slightly exceeded the control limit, the samples can be considered of questionable integrity but are usable for the MWQI study. Another batch was found to have a calcium duplicate sample difference of 0.9 mg/L which significantly exceeded the precision control limit of 0.53 mg/L. Environmental calcium data associated with this batch will be excluded from the MWQI database.

TRIP BLANKS

Trip or field blanks are samples of analyte-free media taken from the laboratory to the sampling site and returned unopened. Their purpose is to measure cross-contamination from the container and preservative during field transport, field handling and storage.

I. ENSECO

Ninety-six trip blanks were analyzed by Enseco. These samples were analyzed for TOC, bromoform, bromodichloromethane, chloroform, and dibromochloromethane. Eight samples were found to have TOC concentrations which were greater than 10 percent of the smallest environmental sample concentration in their respective batch.

II. PACE

No trip blanks were sent to Pace.

III. BRYTE

No trip blanks were sent to Bryte. The practice of requiring trip blanks for trace metals by Bryte was incorporated after the five-year study period.

FIELD DUPLICATES

Field duplicates are two separate samples collected at the same time and placed under identical circumstances. Analysis of these duplicates gives a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures. Field duplicates were collected occasionally by MWQI prior to 1989. Since 1989, these samples were taken regularly. Enseco, Pace and Bryte laboratories performed 4,256 analyses on field duplicate samples submitted by MWQI during the study period. This is a substantial amount of quality control data. A total of 45 different analyses were performed for these duplicates. Overall, 96 percent of MWQI field duplicates are within precision limits.

MWQI used adjusted-Relative Percent Difference limits to evaluate field duplicates instead of using a fixed-RPD limit. Adjusted-RPD limits are dependent on the average concentration and the average reporting limit of the two measurements. These limits can be described by the mathematical function:

$$y = \max(100\%/x, \text{LCS RPD limit})$$

where y is the relative percent difference, x is equal to the average duplicate concentration divided by the average reporting limit, and the LCS RPD limit is taken from LCS duplicate analysis results. Thus, the function takes into consideration the increasing uncertainty of measurements as the concentration approaches the reporting limit.

Field duplicate results for alkalinity, dissolved arsenic, barium, boron, dissolved and total cadmium, dissolved and total chromium, dissolved and total copper, electrical conductivity, dissolved and total lead, lithium, magnesium, total nickel, total selenium, dissolved and total silver, $\text{UVA}_{254 \text{ nm}}$, and total zinc show the highest precision of all the parameters analyzed. Each of these parameters had less than two percent of their RPDs in exceedance of their respective limits.

Parameters that are of intermediate precision (2 to 10 percent of duplicates exceeding RPD limits) are bromide, bromodichloromethane, bromoform, calcium, chloride, chloroform, dibromochloromethane, hardness, dissolved nickel, dissolved organic carbon, potassium, dissolved selenium, sodium, dissolved solids, sulfate, and suspended solids.

The group of field duplicates that has a relatively high frequency of RPD limit exceedances (greater than 10 percent) are total arsenic, color, iron, manganese, total organic carbon, turbidity, and dissolved zinc. However, the results for total arsenic, iron, manganese, and dissolved zinc field duplicates may not be statistically significant due to their relatively small sample sizes. Results of color analysis also shows low precision; however, visual colorimetric techniques are the basis of this quantification and may not be very precise. Note that hardness is calculated by the addition of calcium and magnesium concentrations via quantification of these elements by EPA 215.1 & 242.1 respectively.

Figures B-9 to B-56 illustrate the distribution of RPDs for each analyte. Note that DWR's Bryte Chemical Laboratory analyzed all MWQI field duplicate samples except for THMs and TOC samples which are analyzed by Enseco and Pace.

Field Duplicate Measurements as Related to the MWQI Acceptance Criteria

Figure B-9: Distribution of Field Duplicate RPD's for Alkalinity (EPA 310.1)

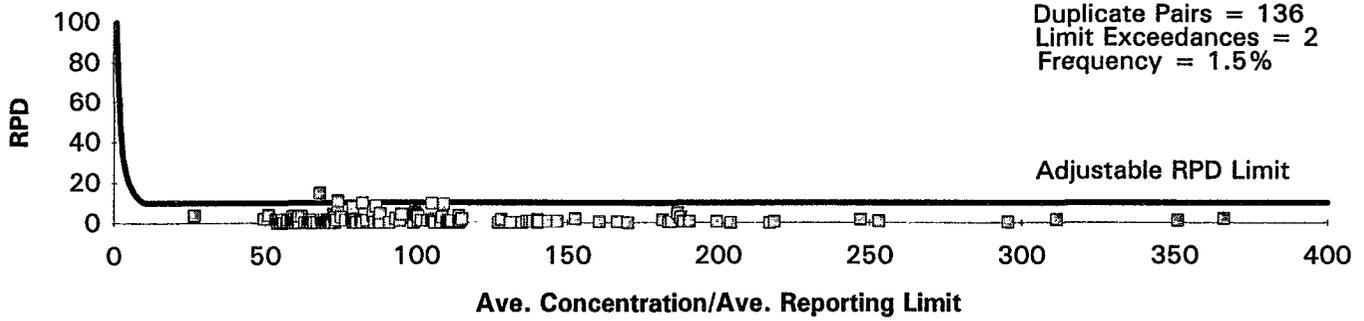


Figure B-10: Distribution of Field Duplicate RPD's for Dissolved Arsenic (EPA 206.3)

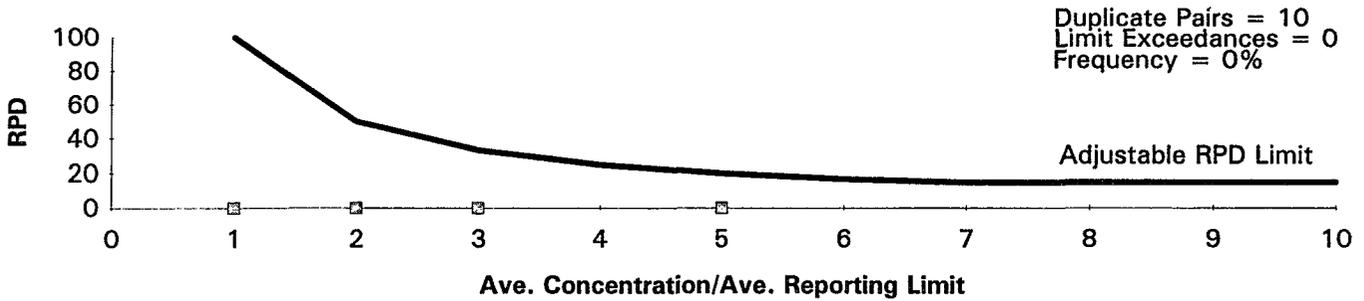


Figure B-11: Distribution of Field Duplicate RPD's for Total Arsenic (EPA 206.3)

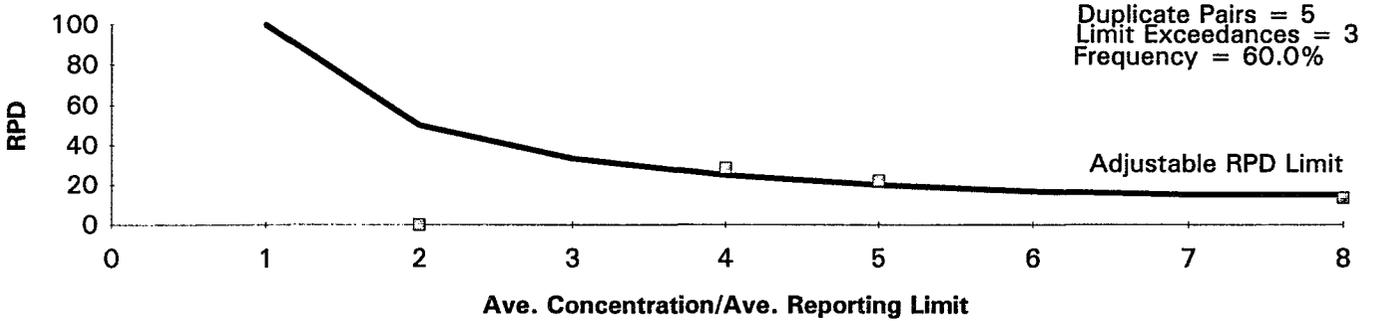
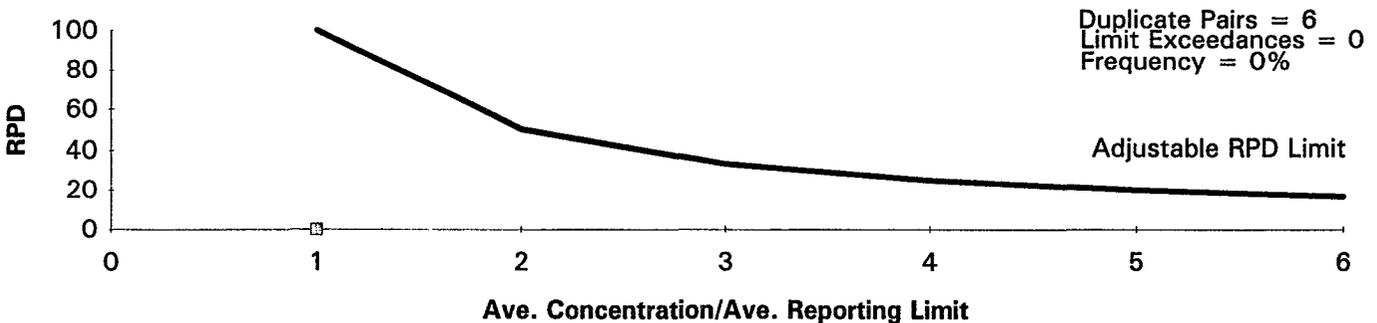


Figure B-12: Distribution of Field Duplicate RPD's for Barium (EPA 208.1)



DWR's Bryte Chemical Laboratory performed all field duplicate analyses except for THMs

B-26

Figure B-13: Distribution of Field Duplicate RPD's for Boron (USGS I-2115-85)

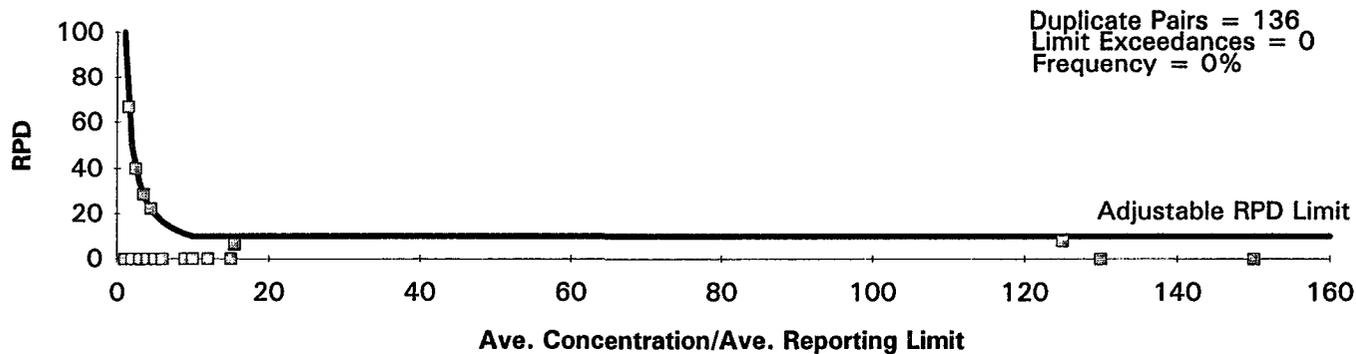


Figure B-14: Distribution of Field Duplicate RPD's for Bromide (EPA 320.1)

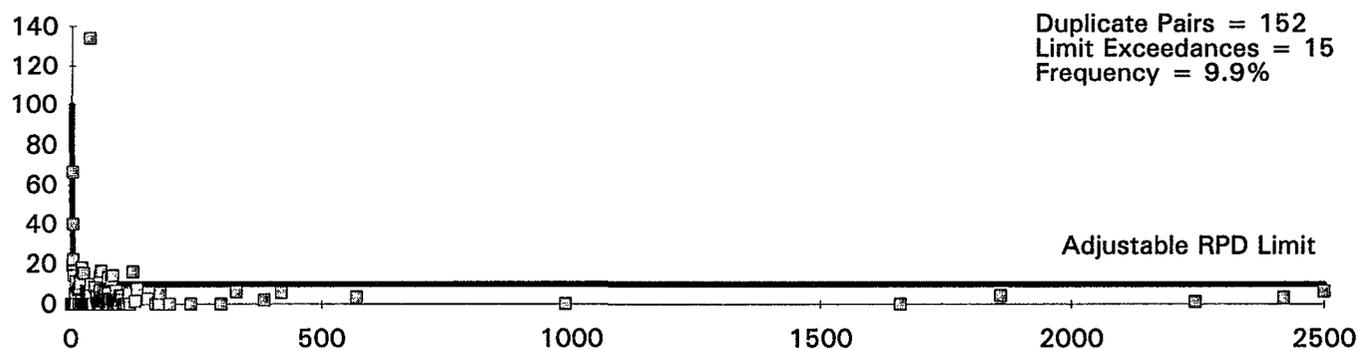


Figure B-15: Distribution of Enseco Field Duplicate RPD's for Bromodichloromethane (EPA 501)

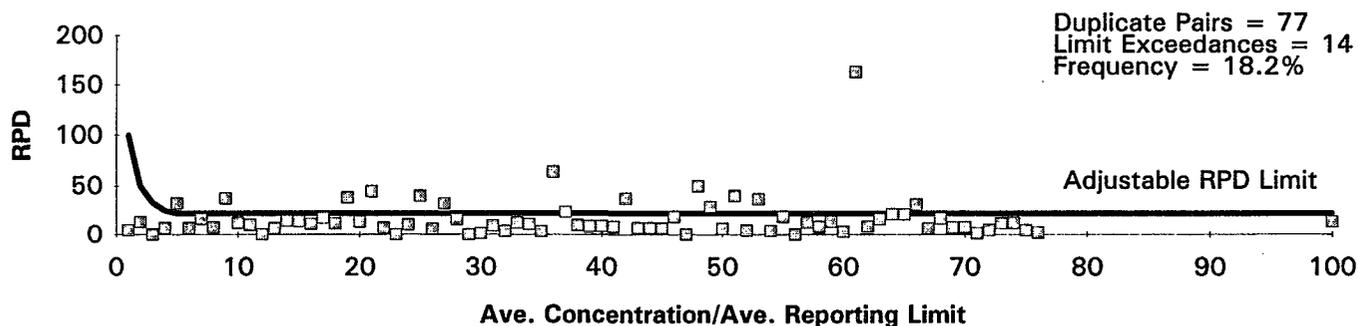


Figure B-16: Distribution of Pace Field Duplicate RPD's for Bromodichloromethane (EPA 601)

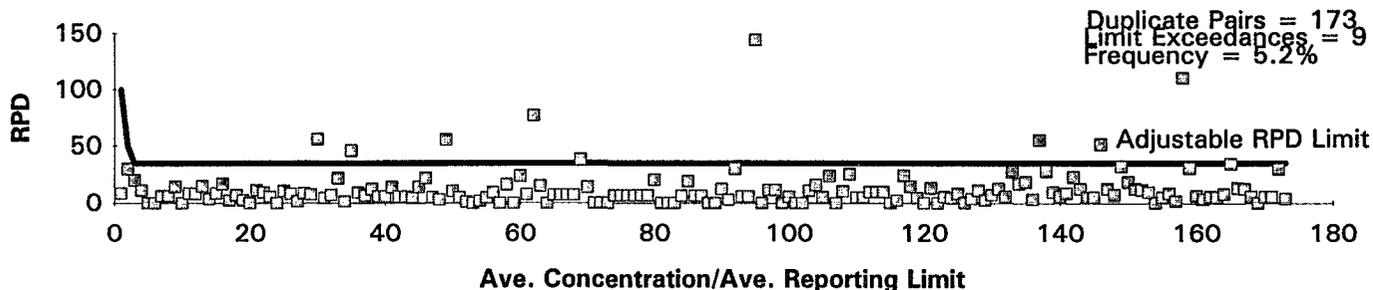


Figure B-17: Distribution of Enseco Field Duplicate RPD's for Bromoform (EPA 501)

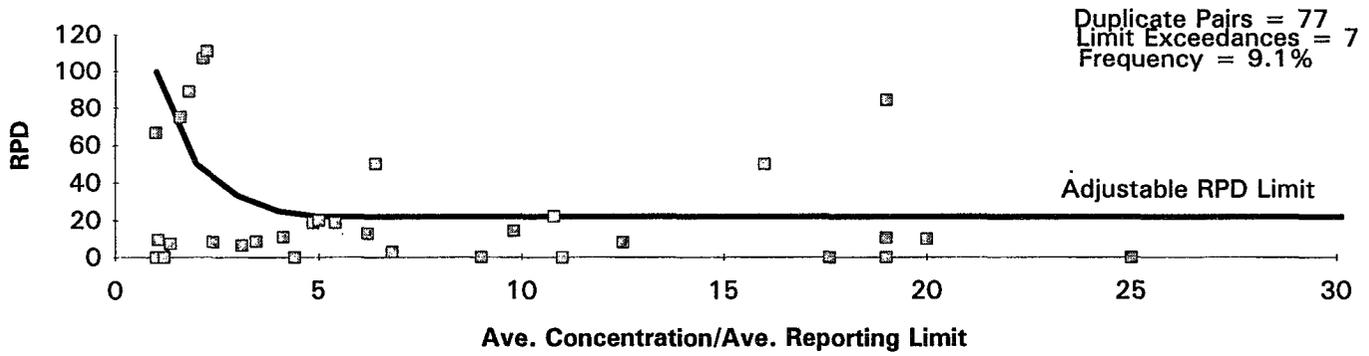


Figure B-18: Distribution of Pace Field Duplicate RPD's for Bromoform (EPA 601)

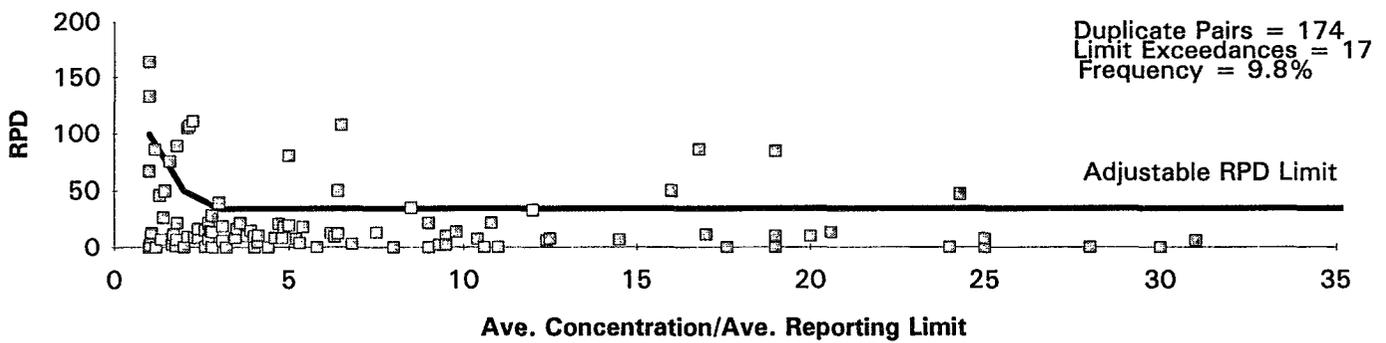


Figure B-19: Distribution of Field Duplicate RPD's for Dissolved Cadmium (EPA 213.2)

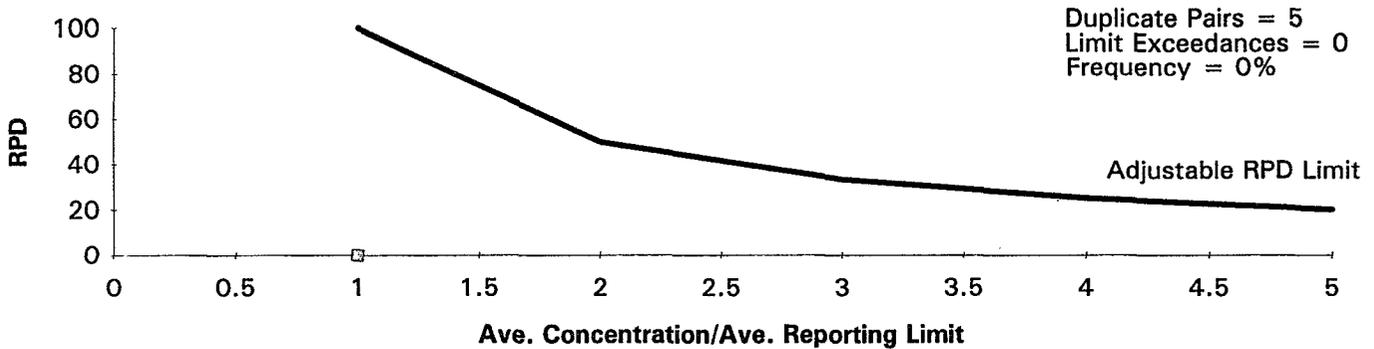


Figure B-20: Distribution of Field Duplicate RPD's for Total Cadmium (EPA 213.2)

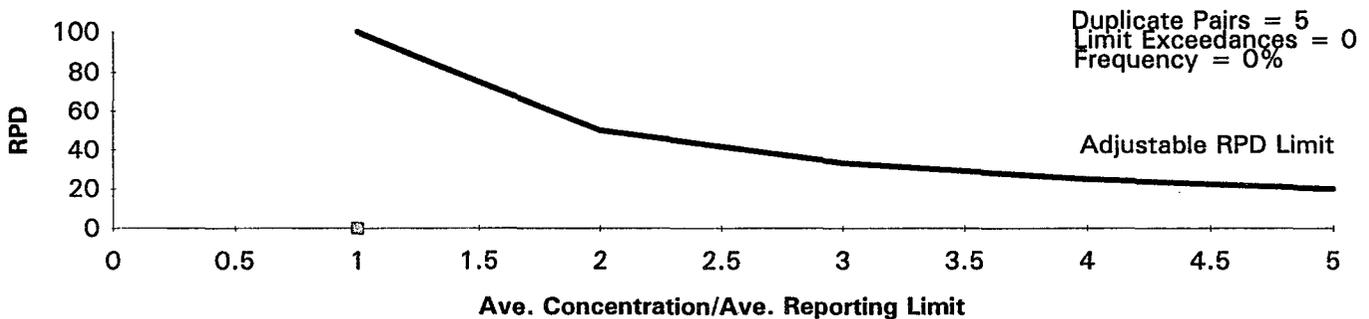


Figure B-21: Distribution of Field Duplicate RPD's for Calcium (EPA 215.1)

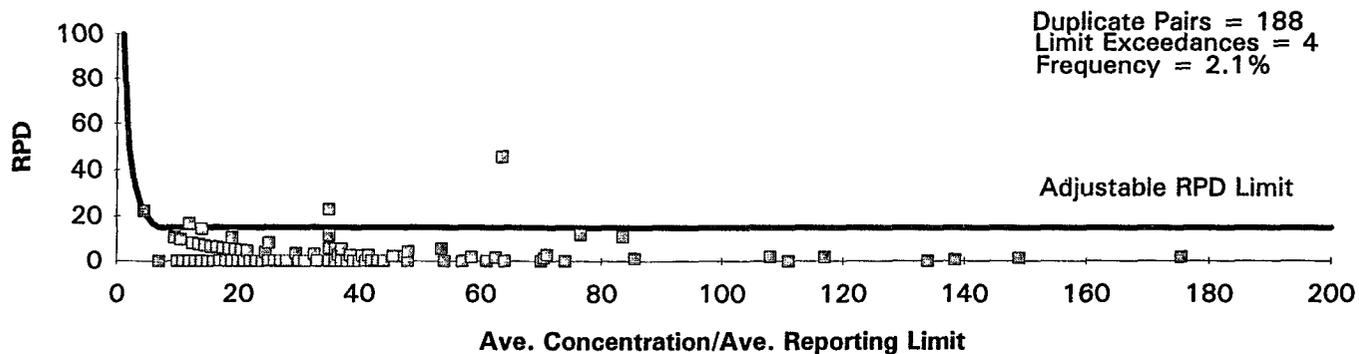


Figure B-22: Distribution of Field Duplicate RPD's for Chloride (EPA 325.2)

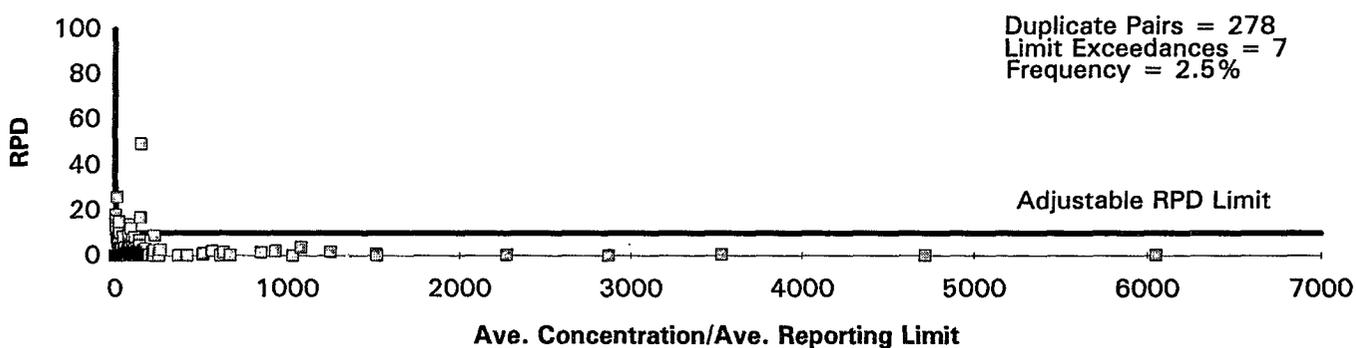


Figure B-23: Distribution of Enseco Field Duplicate RPD's for Chlorodibromomethane (EPA 501)

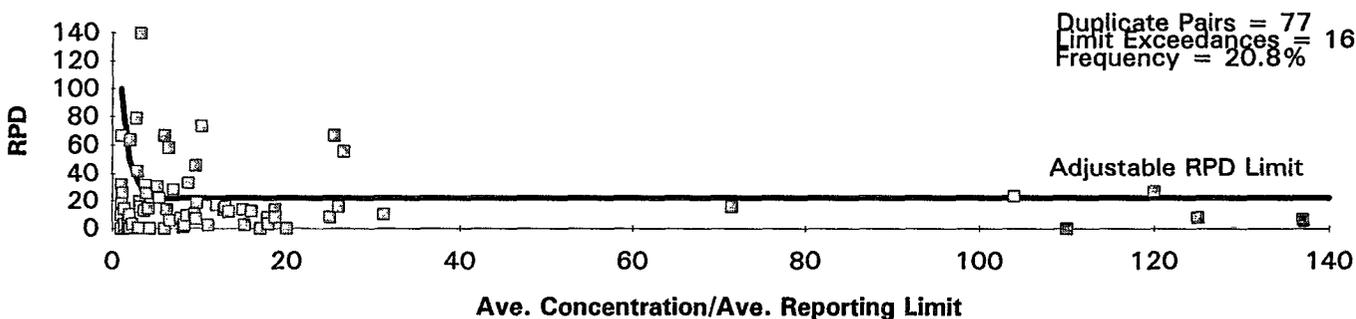


Figure B-24: Distribution of Pace Field Duplicate RPD's for Chlorodibromomethane (EPA 601)

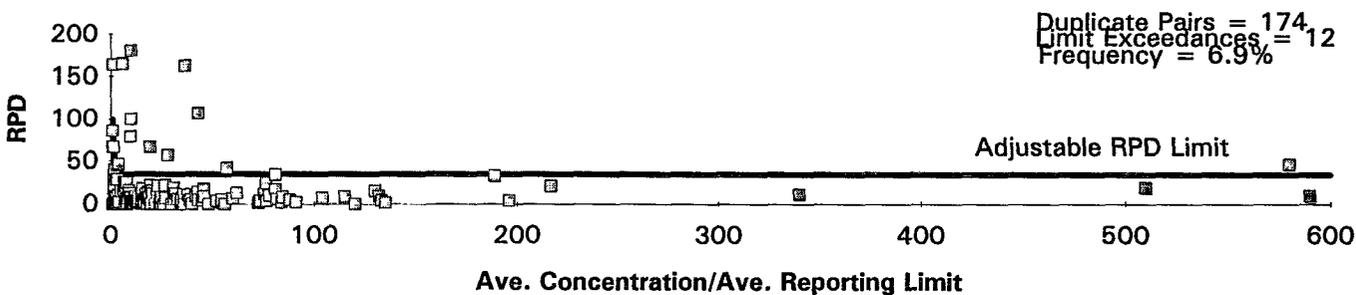


Figure B-25: Distribution of Enseco Field Duplicate RPD's for Chloroform (EPA 501)

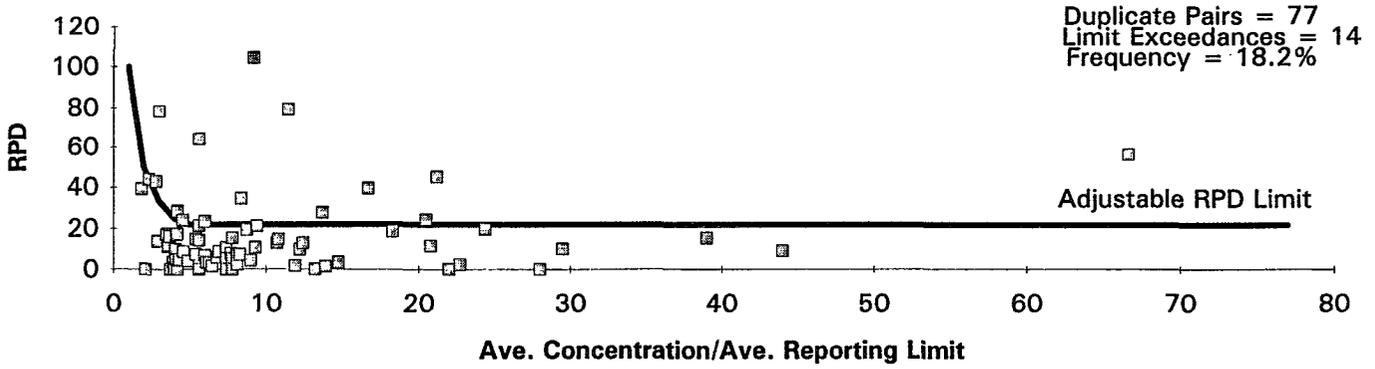


Figure B-26: Distribution of Pace Field Duplicate RPD's for Chloroform (EPA 601)

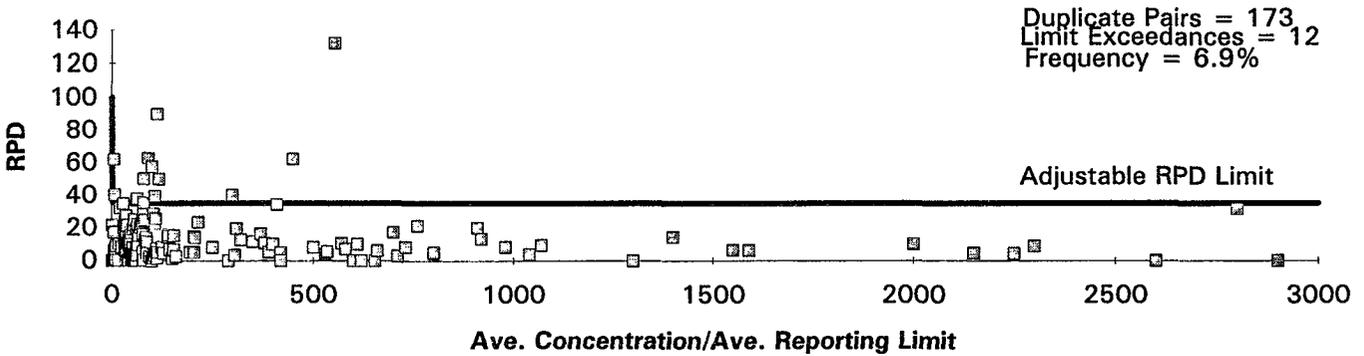


Figure B-27: Distribution of Field Duplicate RPD's for Dissolved Chromium (EPA 218.2)

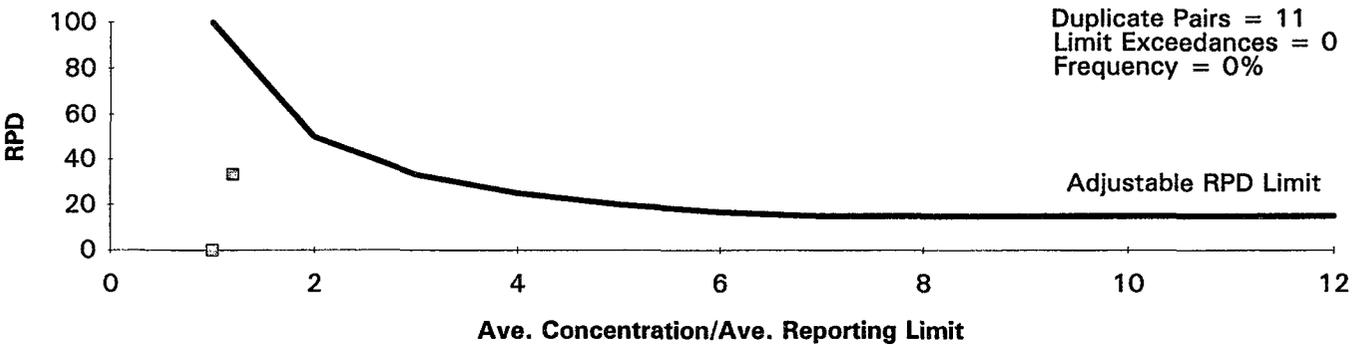


Figure B-28: Distribution of Field Duplicate RPD's for Total Chromium (EPA 218.2)

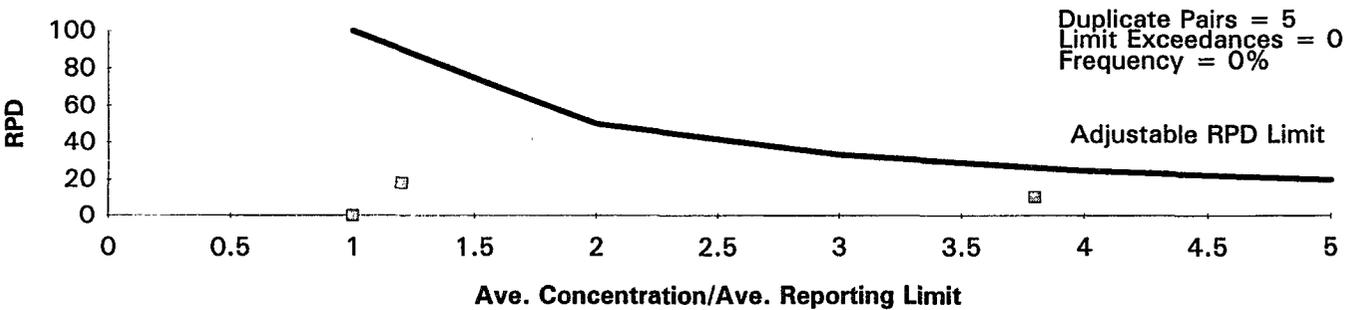


Figure B-29: Distribution of Field Duplicate RPD's for Color (EPA 110.2)

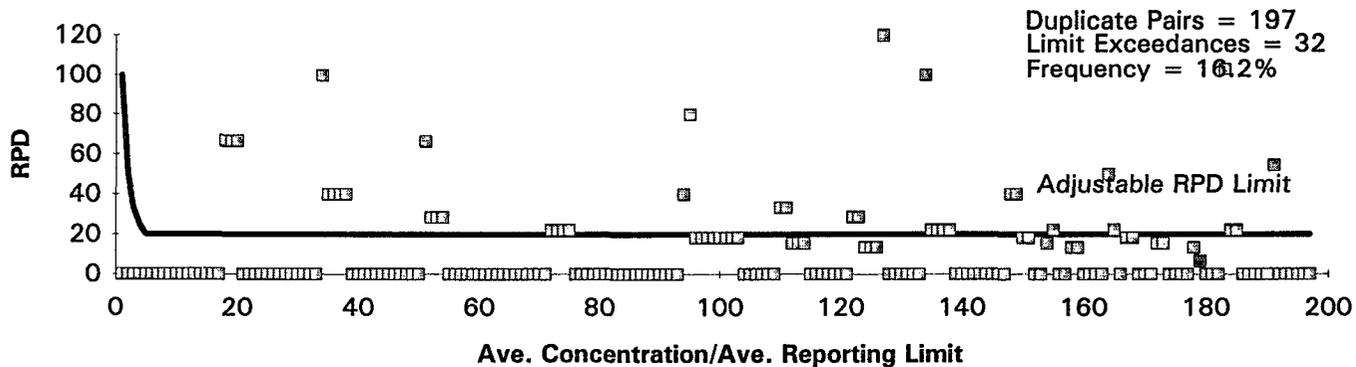


Figure B-30: Distribution of Field Duplicate RPD's for Dissolved Copper (EPA 220.2)

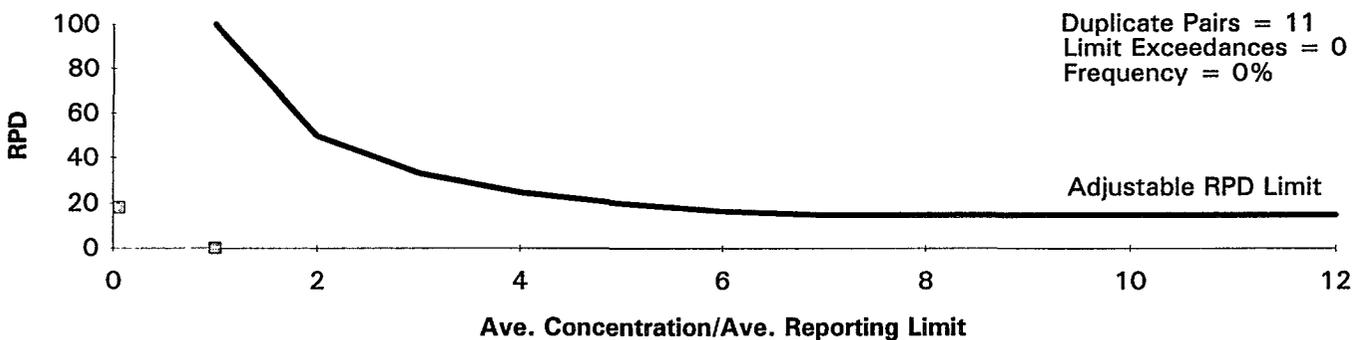


Figure B-31: Distribution of Field Duplicate RPD's for Total Copper (EPA 220.2)

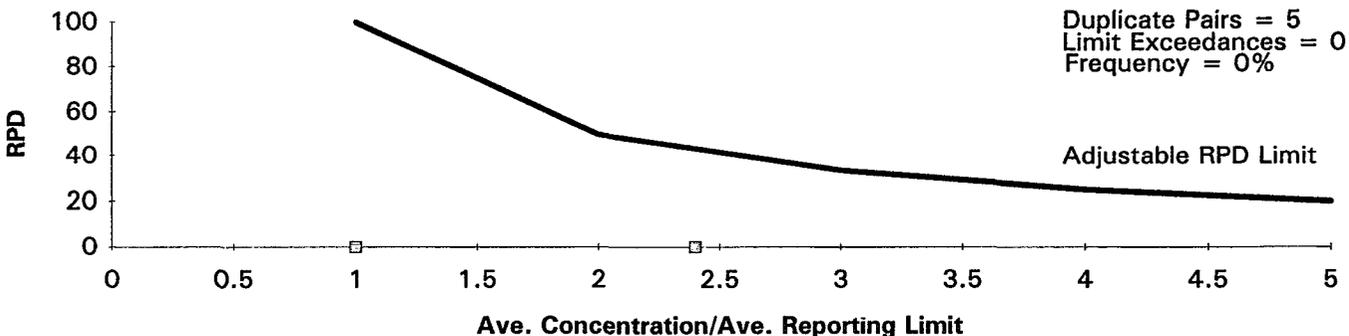
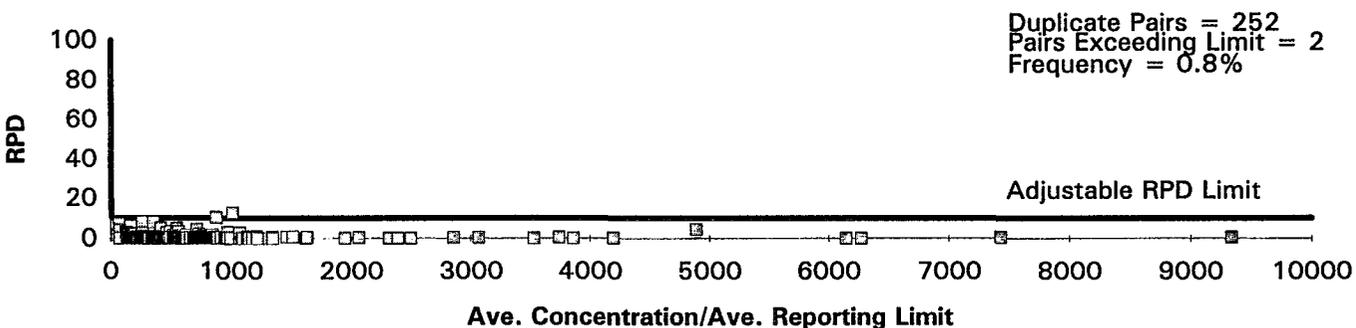


Figure B-32: Distribution of Field Duplicate RPD's for Electrical Conductivity (EPA 120.1)



DWR's Bryte Chemical Laboratory performed all field duplicate analyses except for THMs

B-31

Figure B-33: Distribution of Field Duplicate RPD's for Hardness (EPA 130.2)

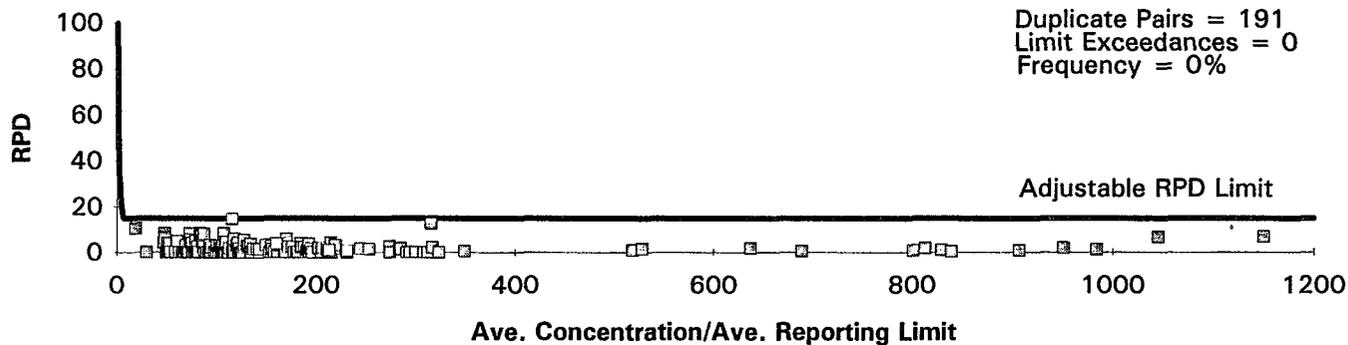


Figure B-34: Distribution of Field Duplicate RPD's for Iron (EPA 236.2)

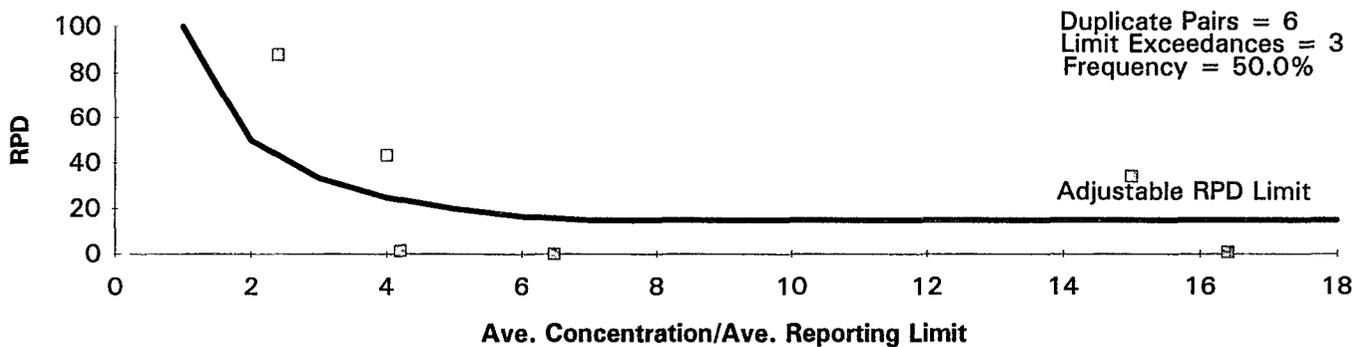


Figure B-35: Distribution of Field Duplicate RPD's for Dissolved Lead (EPA 239.2)

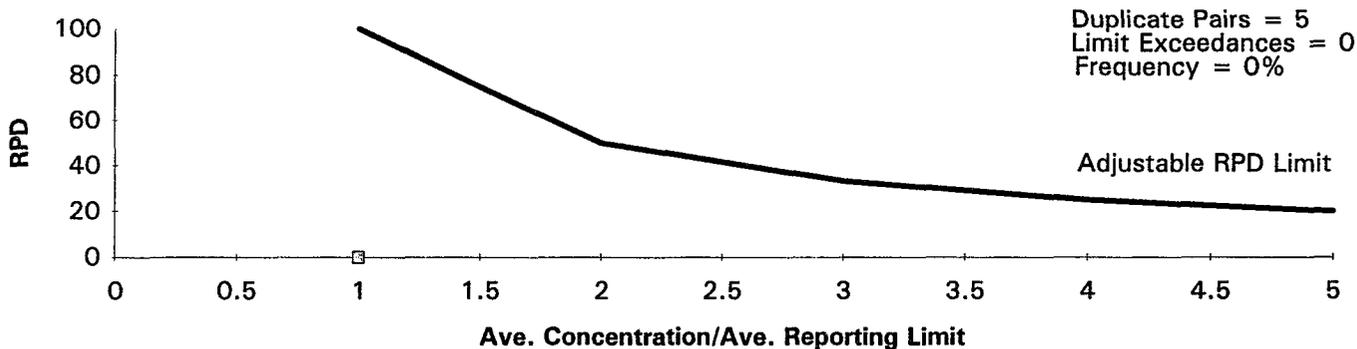


Figure B-36: Distribution of Field Duplicate RPD's for Total Lead (EPA 239.2)

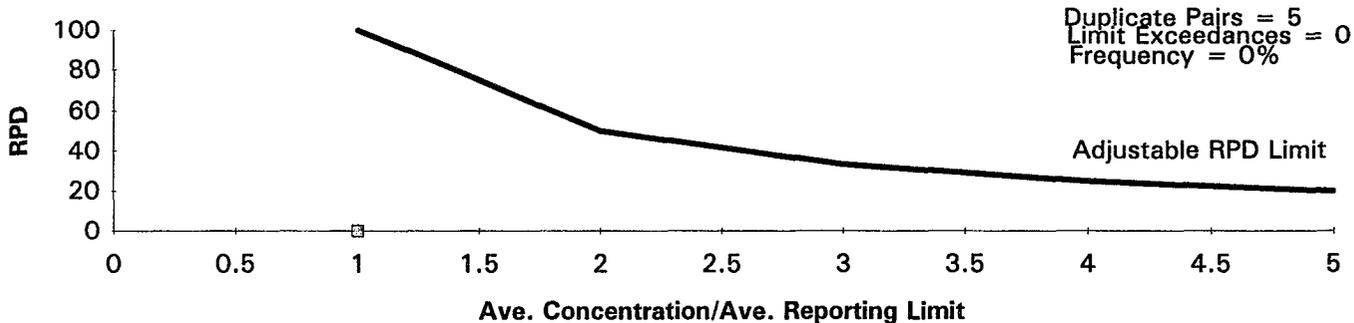


Figure B-37: Distribution of Field Duplicate RPD's for Lithium (USGS I-1425-85)

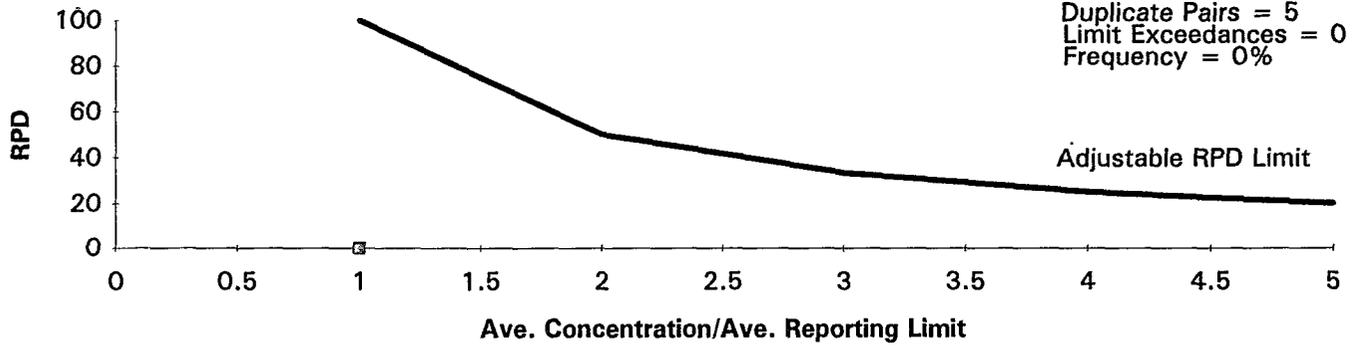


Figure B-38: Distribution of Field Duplicate RPD's for Magnesium (EPA 242.1)

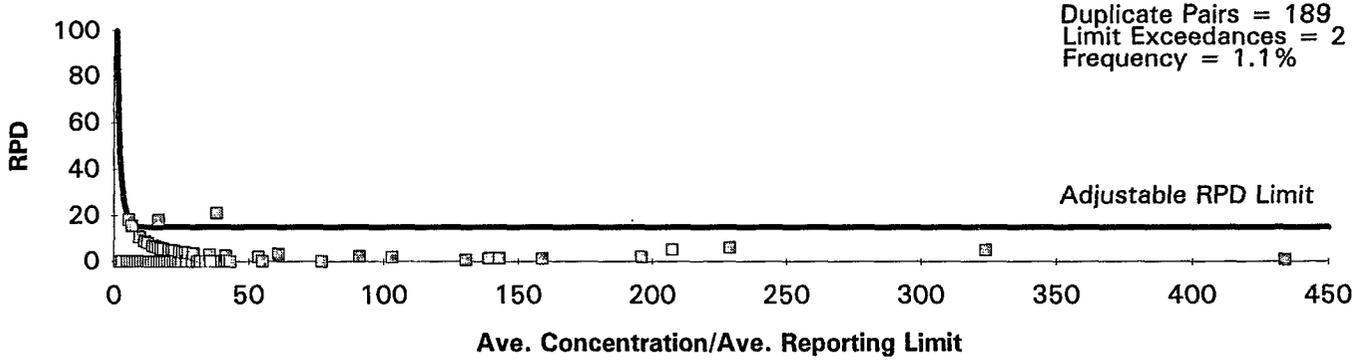


Figure B-39: Distribution of Field Duplicate RPD's for Manganese (EPA 243.2)

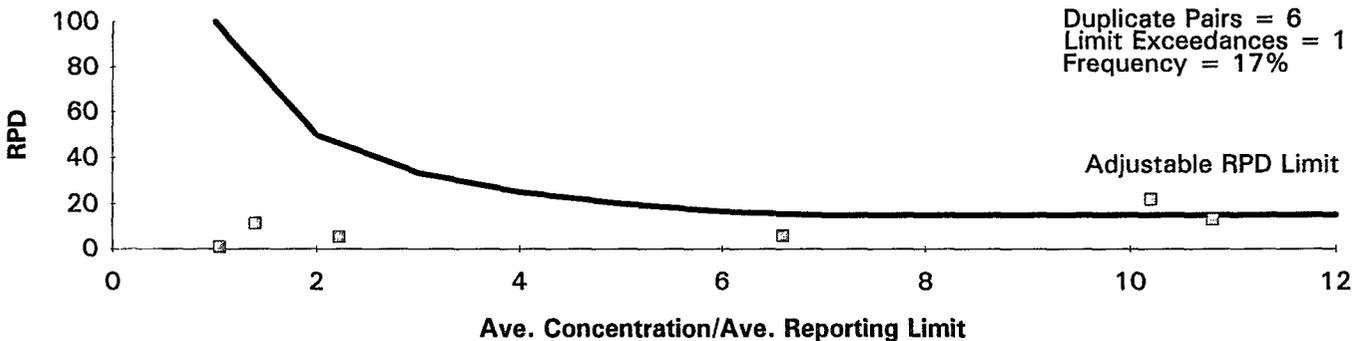


Figure B-40: Distribution of Field Duplicate RPD's for Dissolved Nickel (EPA 246.2)

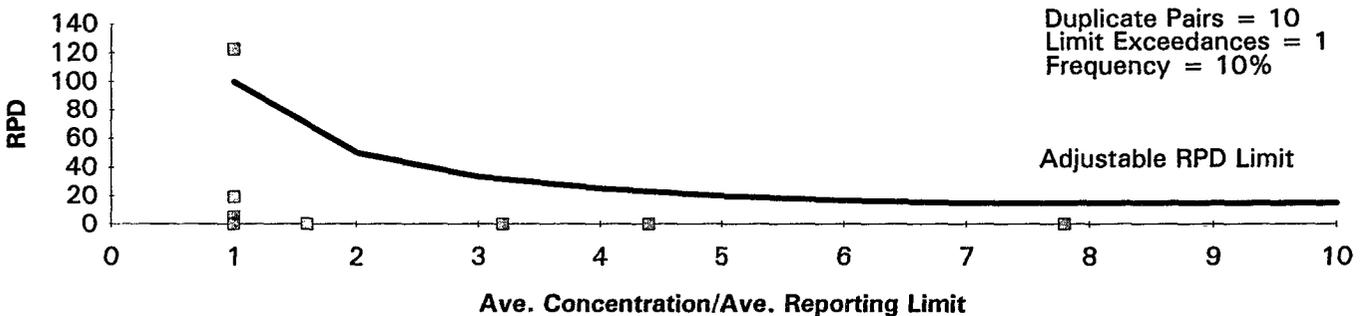


Figure B-41: Distribution of Field Duplicate RPD's for Total Nickel (EPA 249.2)

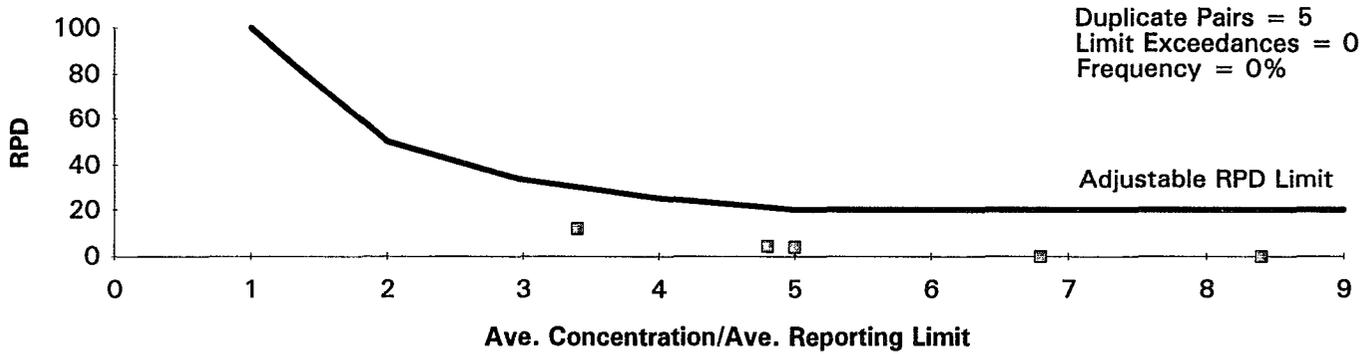


Figure B-42: Distribution of Field Duplicate RPD's for Dissolved Organic Carbon (EPA 415.1)

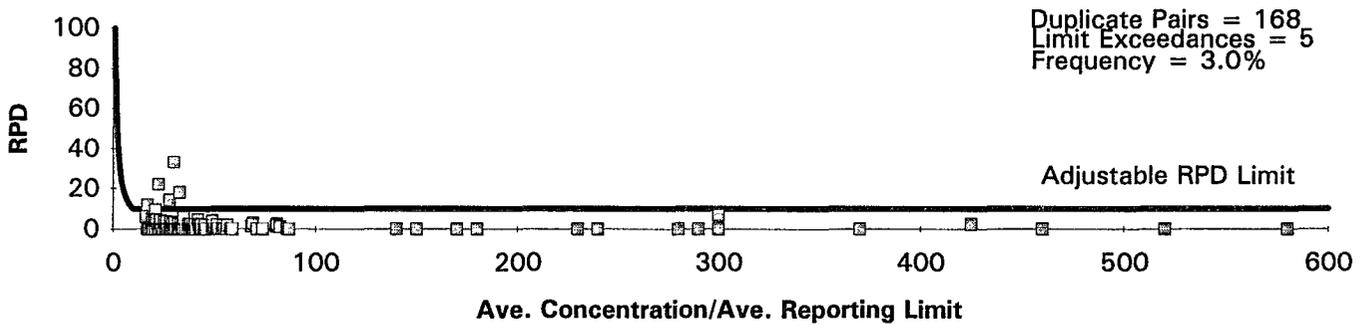


Figure B-43: Distribution of Field Duplicate RPD's for Total Organic Carbon (EPA 415.1)

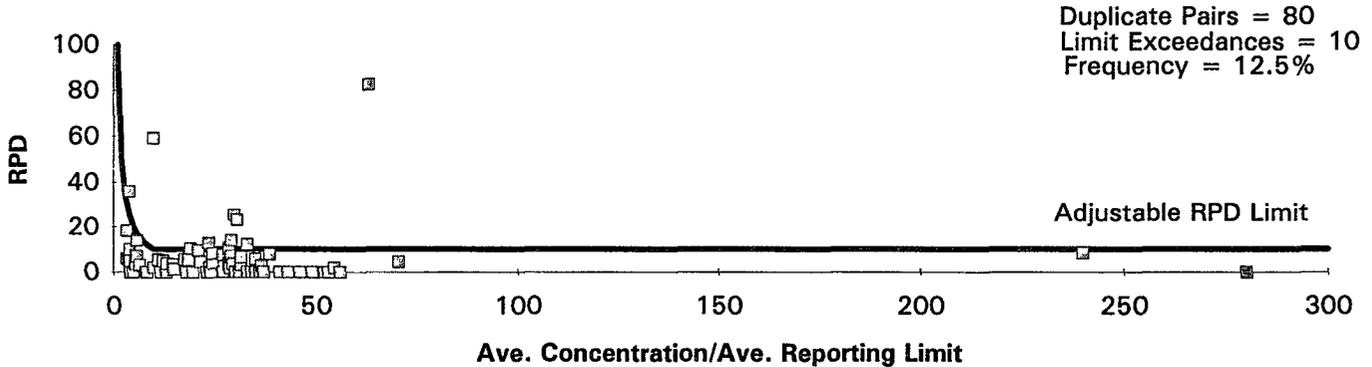
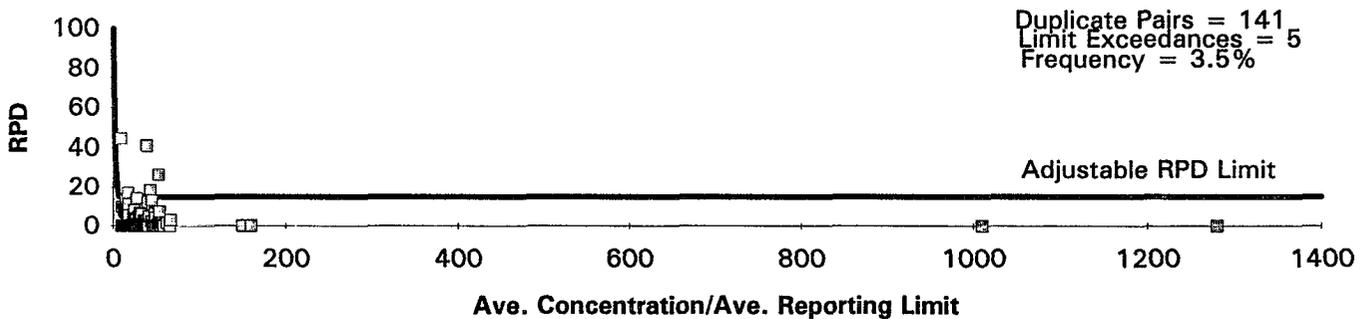


Figure B-44: Distribution of Field Duplicate RPD's for Potassium (EPA 258.1)



DWR's Bryte Chemical Laboratory performed all field duplicate analyses except for THMs

B-34

Figure B-45: Distribution of Field Duplicate RPD's for Dissolved Selenium (EPA 270.3)

Figure B-45: Distribution of Field Duplicate RPD's for Dissolved Selenium (EPA 270.3)

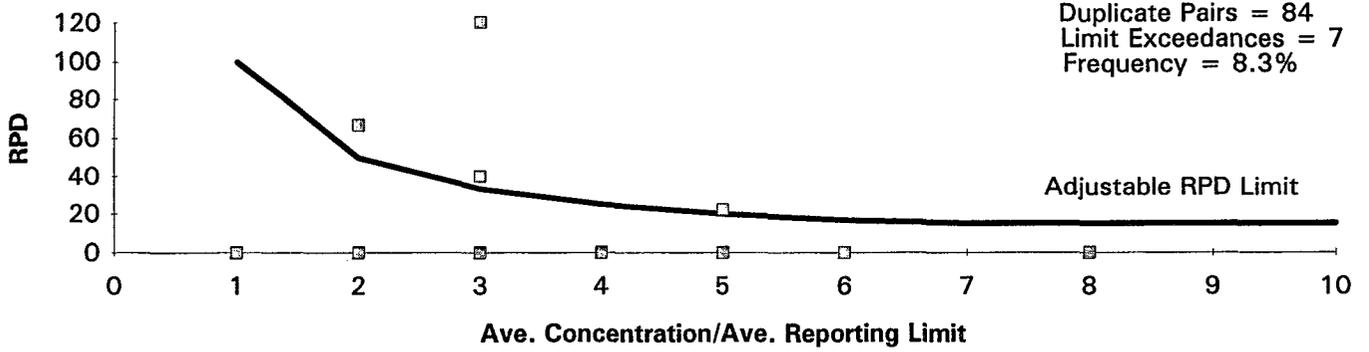


Figure B-46: Distribution of Field Duplicate RPD's for Total Selenium (EPA 270.3)

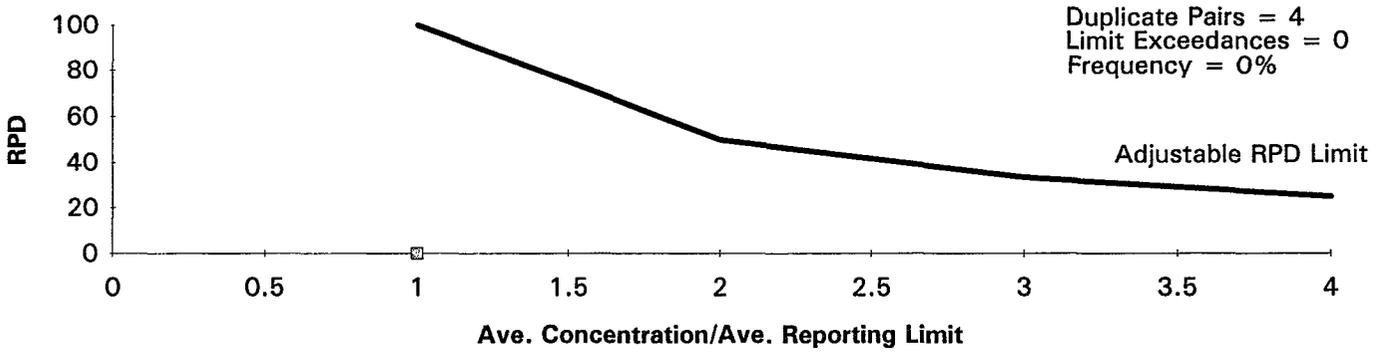


Figure B-47: Distribution of Field Duplicate RPD's for Dissolved Silver (EPA 272.2)

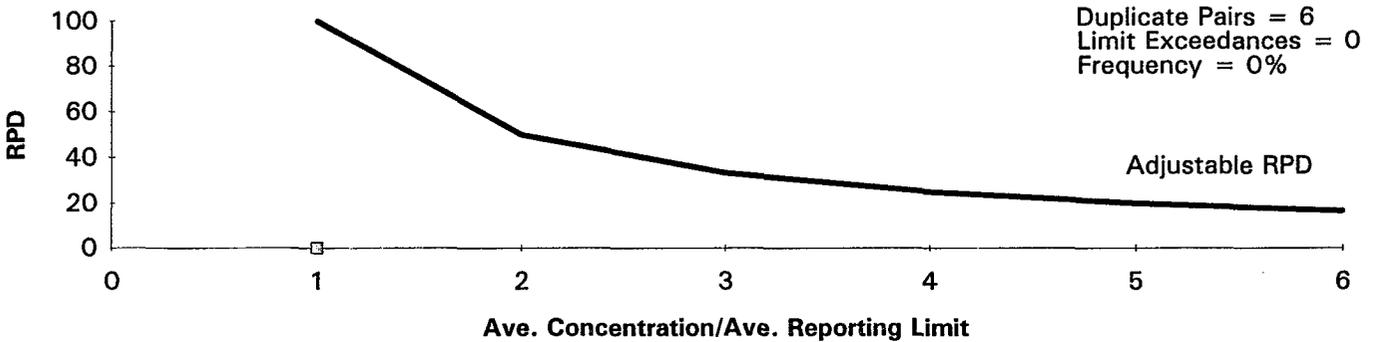


Figure B-48: Distribution of Field Duplicate RPD's for Total Silver (EPA 272.2)

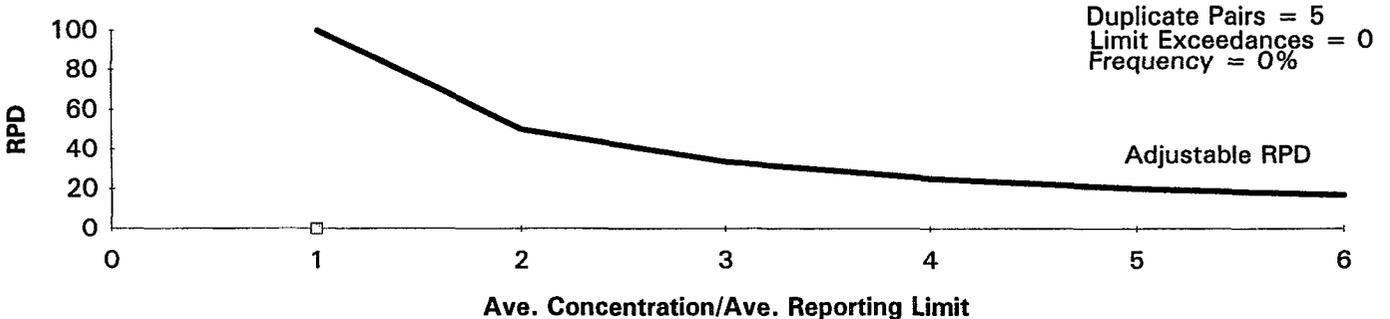


Figure B-49: Distribution of Field Duplicate RPD's for Sodium (EPA 273.1)

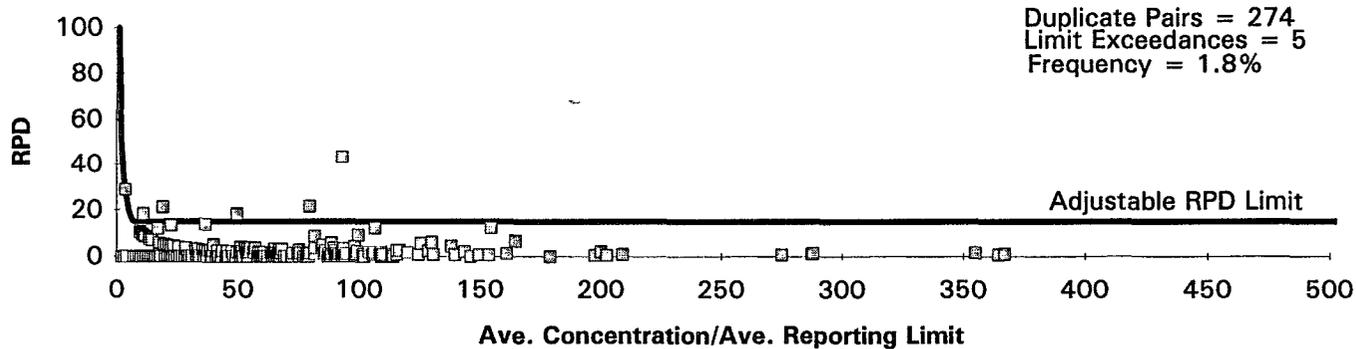


Figure B-50: Distribution of Field Duplicate RPD's for Dissolved Solids (EPA 160.1)

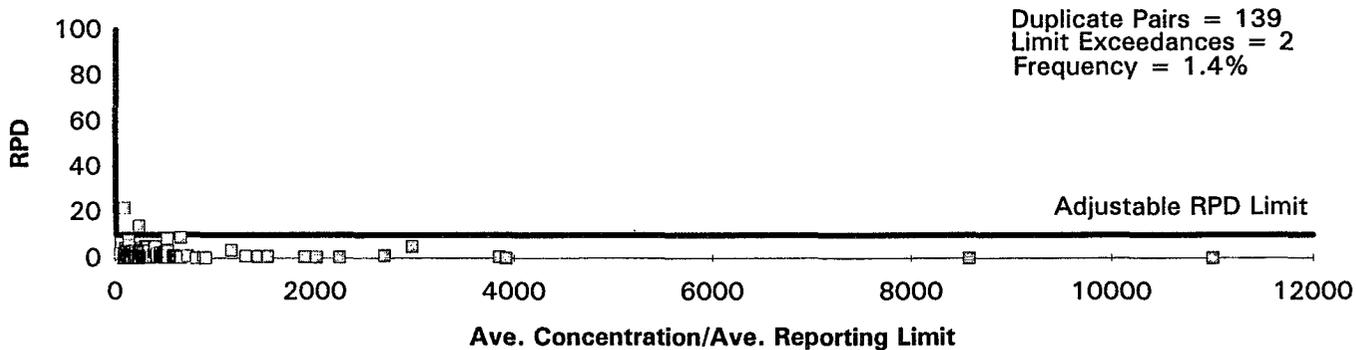


Figure B-51: Distribution of Field Duplicate RPD's for Sulfate (EPA 375.2)

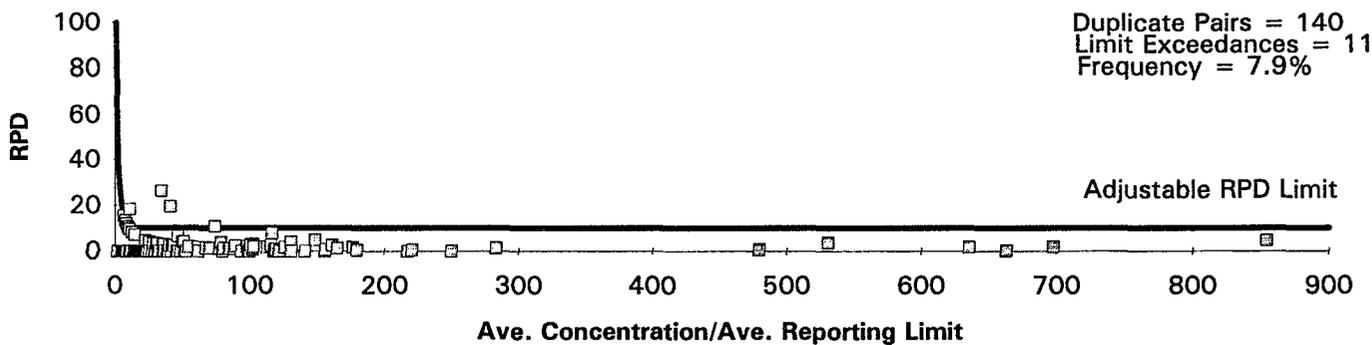


Figure B-52: Distribution of Field Duplicate RPDs for Suspended Solids (EPA 160.2)

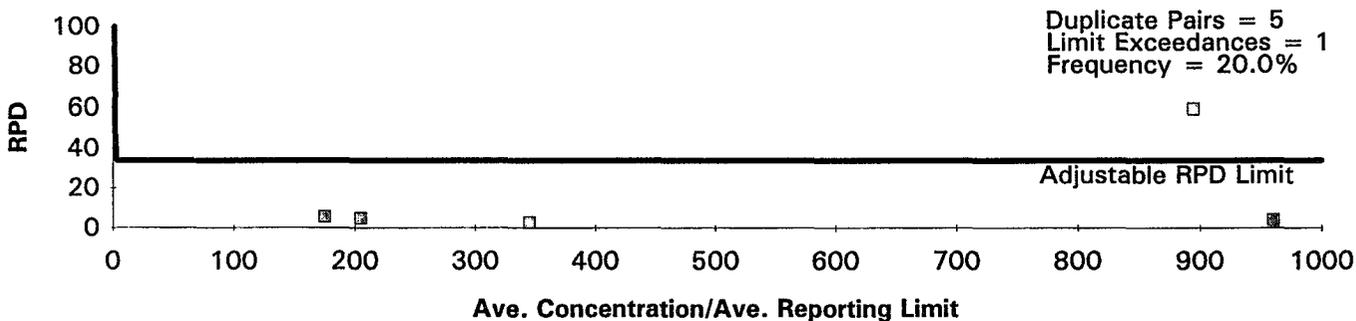


Figure B-53: Distribution of Field Duplicate RPD's for Turbidity (EPA 180.1)

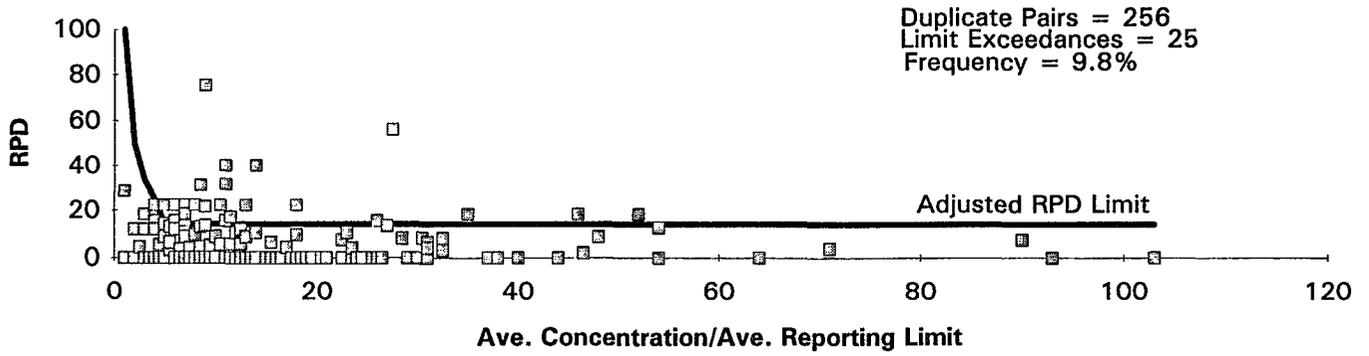


Figure B-54: Distribution of Field Duplicate RPD's for Ultraviolet Absorbtion (254 nm)

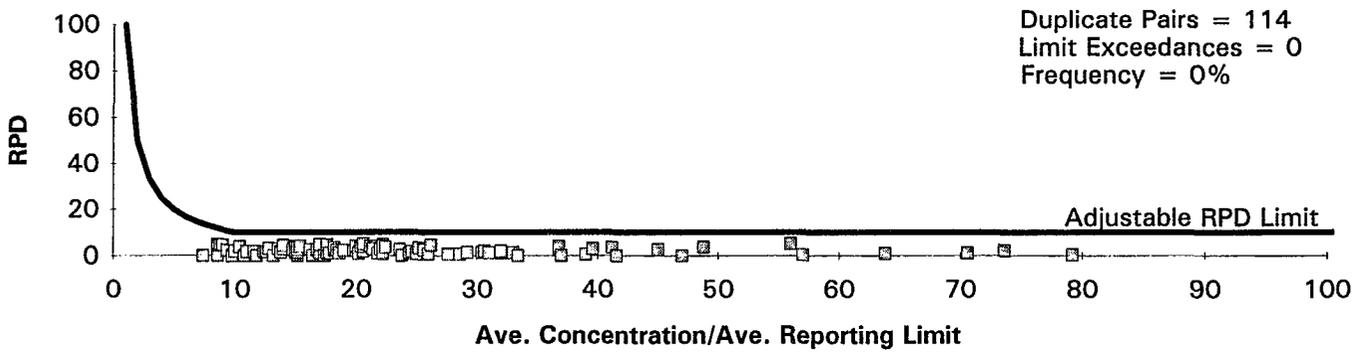


Figure B-55: Distribution of Field Duplicate RPD's for Dissolved Zinc (EPA 289.2)

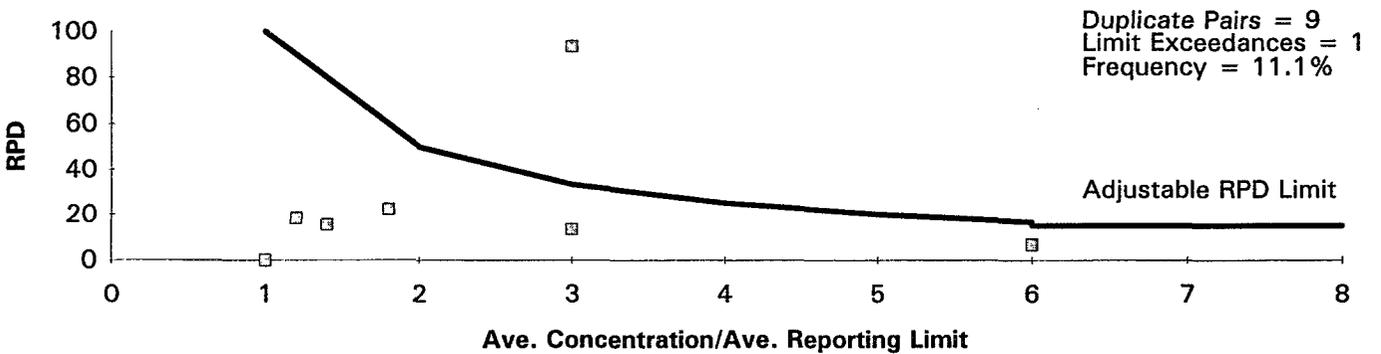


Figure B-56: Distribution of Field Duplicate RPD's for Total Zinc (EPA 289.2)

